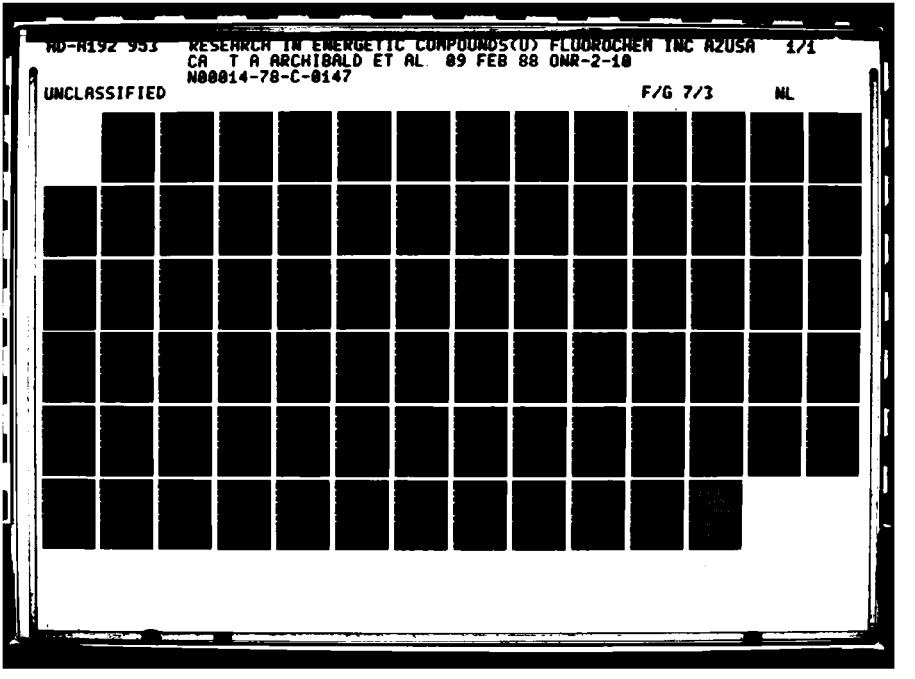
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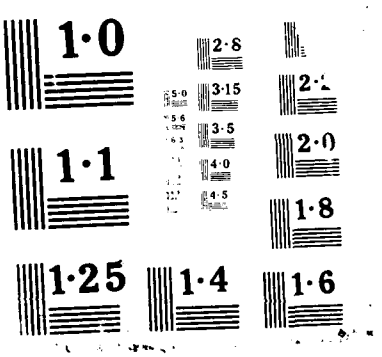
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REPORT No. ONR-2-10 (Final)

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February 1988

FLUOROCHEM, INC.

680 South Ayon Avenue
Azusa, California 91702

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RESEARCH IN ENERGETIC COMPOUNDS

by

T. G. Archibald, L. C. Garver, A. A. Malik,
F. O. Bonsu, D. D. Tzeng, S. B. Preston and K. Baum

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Alternate routes to 1,1,3,3-tetranitrocyclobutane were investigated. Attempts to nitrate or dephenylate 1,3-dinitro-2,4-diphenylcyclobutane were unsuccessful. Ethyl 1,3-dinitrocyclobutane-1-carboxylate, obtained from ethyl bicyclo[1.1.0]butane-1-carboxylate and dinitrogen tetroxide, was treated with silver nitrate, sodium nitrite and base to give 1,1,3,3-tetranitrocyclobutane in 10 to 22% yield. 3,3-Dinitrocyclobutanecarboxylic acid, obtained *via* ethyl 3-oxocyclobutane-1-carboxylate oxime, was subjected to a Curtius reaction, conversion of the isocyanate to the amine, and oxidation to give 1,1,3-trinitrocyclobutane. This compound decomposed under oxidative nitration conditions. Attempts to oxidize 3,3-dinitrocyclobutanol, obtained from the amine, were unsuccessful. 3,3-Dinitrocyclobutane-1,1 dicarboxylic acid was prepared from diethyl 3-oxocyclobutane-1,1-dicarboxylate. (Continued)

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The synthesis of spiro joined nitrocyclobutanes was investigated. Ketene dimerization of 3-methylenecyclobutanecarboxylic acid, followed by ozonization gave 2,5,8,10-tetraoxo[3.1.3.1]decane. Chlorination of the tetraoxime and reductive dechlorination gave 2,5,8,10-tetranitrodispiro-[3.1.3.1]decane.

Process improvements in the synthesis of 1,3,3-trinitroazetidine (TNAZ) were studied. Yields of 1-*t*-butyl-3-hydroxyazetidine from *t*-butylamine and epichlorohydrin were increased to 69% by condensing the reagents in hexane and cyclizing in acetonitrile. The crude mesylate was purified by trituration with ether. The yield of the nitrite displacement to give 1-*t*-butyl-3-nitroazetidine was increased to 55-65% by using a two phase (water, Freon 113) medium. 1-*t*-Butyl-3,3-dinitroazetidine, obtained by the persulfate oxidative nitration, was nitrolyzed with nitric acid and trifluoroacetic acid in methylene chloride to give TNAZ in 95-98% yield.

Work was continued on nitro-substituted fluorinated monomers. Reactions of α,ω-diiodoperfluoroalkanes with ethylene, followed by nitrite displacement gave the α,ω-dinitro compounds, $O_2N-CH_2CH_2(CF_2)_nCH_2CH_2-NO_2$, where n = 4, 6, 8. Reactions of the nitronate salts (n = 4, 6) with tetranitromethane gave the tetranitro compounds, $(NO_2)_2CHCH_2(CF_2)_nCH_2CH(NO_2)_2$, which reacted with formaldehyde and methyl acrylate, respectively, to give the diols, $HOCH_2C(NO_2)_2CH_2(CF_2)_nCH_2C(NO_2)_2CH_2OH$, and esters, $MeO_2CCH_2CH_2-C(NO_2)_2CH_2(CF_2)_nCH_2C(NO_2)_2-CH_2CH_2CO_2Me$. Reactions of the α,ω-dinitro compounds, $O_2N-CH_2CH_2(CF_2)_nCH_2CH_2-NO_2$, with methyl acrylate gave the diadducts or tetra-adducts, depending on conditions.

Work reported in previous interim reports is summarized briefly.

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I. INTRODUCTION

This Final Report summarizes the research that has been conducted under Contract N00014-78-C-0147 during the period 1 January 1978 through 31 December 1987. Detailed experimental procedures and discussion are included for the work performed from 1 January 1987 through 31 December 1987. The earlier work has been detailed in the following Interim Reports:

Fluorochem Report ONR-2-1, 1 January 1978 through 28 February 1979.

Fluorochem Report ONR-2-2, 1 March 1979 through 29 February 1980.

Fluorochem Report ONR-2-3, 1 March 1980 through 31 December 1980.

Fluorochem Report ONR-2-4, 1 January 1981 through 31 December 1981.

Fluorochem Report ONR-2-5, 1 January 1982 through 31 December 1982.

Fluorochem Report ONR-2-6, 1 January 1983 through 31 December 1983.

Fluorochem Report ONR-2-7, 1 January 1984 through 31 December 1984.

Fluorochem Report ONR-2-8, 1 January 1985 through 31 December 1985.

Fluorochem Report ONR-2-9, 1 January 1986 through 31 December 1986.

The following publications in technical journals have been prepared under this contract:

Baum, K.; Lerdal, D.A.; Horn, J.S. *J. Org. Chem.* **1978**, 43, 203. "Synthesis of Organosilanes and Polysiloxanes with Nitro and Fluoro Substituents."

Lerdal, D.A.; Baum, K. *J. Organometallic Chem.* **1978**, *159*, 251. "Synthesis of Bis(3,3-dinitrobutyl)polysiloxanes."

Baum, K.; Guest, A.M. *Synthesis* **1979**, *311*. "Michael Reaction of Methylenemalonates with Nitro Compounds."

Berkowitz, P.T.; Baum, K. *J. Org. Chem.* **1980**, *45*, 4853. "Reactions of 2-Fluoro-2-nitro-1,3-propanediol. Trifluoromethanesulfonates and 3-Fluoro-3-Nitrooxetane."

Berkowitz, P.T.; Baum, K. *J. Org. Chem.* **1981**, *46*, 3816. "Reactions of 2-Fluoro-2-Nitro-1,3-propanediol. p-Toluenesulfonates."

Baum, K.; Berkowitz, P.T.; Grakauskas, V.; Archibald, T.G. *J. Org. Chem.* 1983, *48*, 2953. "Synthesis of Electron-Deficient Oxetanes. 3-Azidooxetane, 3-Nitrooxetane, and 3,3-Dinitrooxetane."

The following manuscripts have been completed and are being submitted:

Archibald, T. G.; Baum, K. "Synthesis of Polynitroadamantanes. Oxidations of Oximinoadamantanes."

Archibald, T. G.; Baum, K.; Gilardi, R.; George, C. "Synthesis and X-ray Crystal Structure of 1,3,3-Trinitro-Substituted Azetidine."

The initial emphasis of the research was on the development of long-chain energetic diols for propellant applications. The chemistry of nitro-oxetanes was pioneered to provide monomers that could be converted to hydroxy-terminated oligomers (Report ONR-2-1). A practical synthesis of 2-fluoro-2-nitropropanediol was developed, and it was found that the monotriflate could be cyclized to the oxetane, although similar non-fluorinated nitro compounds underwent deformylation. A convenient synthesis of 1-fluoronitroethylene was found (Reports ONR-2-2 and ONR-2-3). The polymerization of fluorodinitroethyl glycidyl was studied (Reports ONR-2-2 and ONR-2-3). 2,2-Dinitrooxetane (Reports ONR-2-2 and ONR-2-3) was synthesized from epichlorohydrin by the addition of acetic acid, blocking the alcohol as an acetal, cyclization and hydrolysis to give 3-hydroxy-oxetane, displacement of the tosylate with azide, reduction to the amine, oxidation and oxidative nitration. Polymers of 2,2-dinitrooxetane (Report ONR-2-4) were too high-melting for propellant applications, but potentially useful oligomers were obtained from the intermediate, 3-azidooxetane.

The program was subsequently reoriented to the synthesis of new high-density explosives. Procedures developed for the conversion of 2-adamantanone to 2,2-dinitroadamantane (Report ONR-2-4) were used to synthesize 2,2,6,6-tetranitroadamantane and bicyclononane derivatives

(Report ONR-2-5), but 2,2,4,4-tetranitroadamantane could not be prepared (Report ONR-2-6). The first synthesis of 1,3,3-trinitroazetidine was accomplished by the addition of *t*-butylamine to epichlorohydrin to give 1-*t*-butyl-3-hydroxyazetidine, nitrite displacement of the corresponding methanesulfonate, and nitrolysis of the *t*-butyl group (Report ONR-2-6). 4,4,8,8-Tetranitrobicyclo[3.3.0]-2,6-dioxaoctane was synthesized from 4,8-di-p-tosylatobicyclo[3.3.0]-2,6-dioxaoctane (Report ONR-2-7). 1,1,4,4-Tetranitrocyclobutane was synthesized by a route involving the oxidation of 1,4-diaminocyclobutane and oxidative nitration (Report ONR-2-8).

Another aspect of the program involves the preparation of nitro-substituted fluorocarbons for use as pyrotechnic binder ingredients. The initial approach of adding nitronate salts to 3,3-difluoroacrylates and 2,2-difluorovinyl gave O- rather than C- nitronate adducts; reactions of lithium 2-nitropropane-1,3-diol acetonide with perfluoroalkyl iodides gave the 2-perfluoroalkyl-2-nitropropane-1,3-diol derivatives (Report ONR-2-8). Nitration of the oximes of trifluoromethyl ketones gave the *gem*-dinitro derivatives. Reactions of α,ω-diiodoperfluoroalkanes with ethylene, followed by nitrite displacement gave the α,ω- bis(iodoethyl) derivatives (Report ONR-2-9).

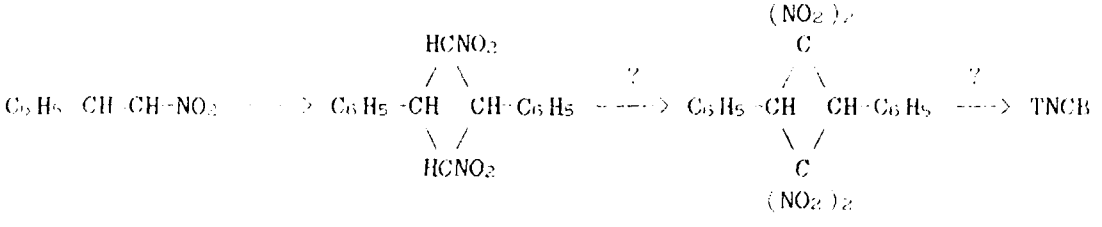
The work performed during the final contract year includes studies aimed at improved routes to 1,1,3,3-tetranitrocyclobutane and nitro-substituted four-membered ring compounds with spiro junctions. Process studies for the scale-up of the preparation of 1,3,3-trinitroazetidine were carried out. Work on the preparation of nitro-substituted fluorocarbons was also continued.

II. POLYNITROCYCLOBUTANES

A. Discussion

1,1,3,3-Tetranitrocyclobutane. In the preceding Interim Report,[1] the first synthesis of 1,1,3,3-tetranitrocyclobutane (TNCB) was described. 1,3-Diaminocyclobutane, prepared by a multistep route, was oxidized with m-chloroperbenzoic acid to give 1,3-dinitrocyclobutane, which was converted to TNCB by oxidative nitration. To enable the preparation of multi-gram samples for testing of this potentially useful explosive, an investigation of alternate synthesis procedures was initiated.

A readily available potential starting material, *trans*-2,4-diphenyl-1,3-dinitrocyclobutane, is prepared by the photodimerization of β-nitrostyrene.[2] Oxidative nitration and oxidative dephenylation would give TNCB directly.



Efforts to effect the oxidative nitration of *trans*-2,4-diphenyl-1,3-dinitrocyclobutane were unsuccessful. Generation of the nitronate salt with methanolic sodium methoxide at 20 °C or n-butyl lithium at -60 °C followed by reaction with tetranitromethane resulted in decomposition. Similar results were obtained in oxidative nitrations using aqueous ferricyanide-persulfate or silver nitrate as the oxidant, or the dinitronate salt generated with butyl lithium or potassium t-butoxide as the substrate.

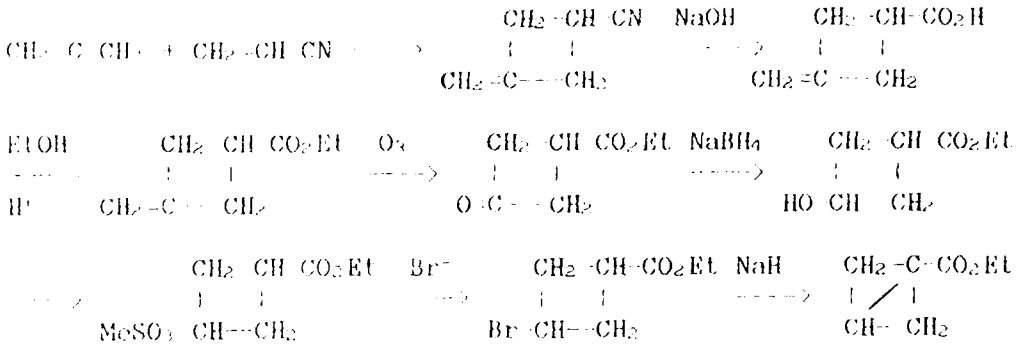
Unsuccessful attempts were made to oxidize the phenyl groups of *trans*-2,4-diphenyl-1,3-dinitrocyclobutane to carboxy groups using ruthenium tetroxide/sodium hypochlorite in aqueous carbon tetrachloride.[3] Loss of aliphatic C-H resonances in the ^{1}H NMR suggested cyclobutane ring chlorination. Use of hydrogen peroxide in trifluoroacetic acid[4] or ozone on silica gel[5] afforded only isomerized starting material. Attempts to prepare 1,3-dibromo-1,3-dinitro-2,4-diphenylcyclobutane by bromination gave the elimination product, 3-bromo-1,*trans*-3-dinitro-2,*trans*-4-diphenylcyclobutene.[6]

An alternate strategy to TNCB based on the 1,3-dipolar addition of electrophiles to bicyclobutanes was investigated subsequently. Bicyclo[1.1.0]butane[7,8,9] was prepared by oxidation of cyclopropylcarbinol to cyclopropylcarboxaldehyde with cerric ammonium nitrate[10] and thermolysis of the corresponding tosyl hydrazone. *Reaction of bicyclobutane with dinitrogen* tetroxide at -50 or -78 °C did not give 1,3-dinitrocyclobutane. Subsequently, 1,3-*diiodocyclobutane*[9], obtained by iodine addition to bicyclo[1.1.0]-butane, was subjected to azide displacement to give 1,3-diazidocyclobutane, characterized by IR and NMR spectra. Hydrogenation of this diazide (72 h, 55 psi H_2 pressure) appeared to give the diamine, but only in very low yield, and oxidation of the crude material with m-chloroperbenzoic acid did not give 1,3-dinitrocyclobutane. Reaction of the diazide with tributylphosphine afforded the bis-phosphine imine[11], but low temperature ozonolyses did not give 1,3-dinitrocyclobutane.

A recent report[12] that dinitrogen tetroxide adds across methyl 1-tricyclo[4.1.0.0^{2,7}]heptanecarboxylate prompted us to investigate the addition of dinitrogen tetroxide to ethyl bicyclo[1.1.0]butane-1-carboxylate. An

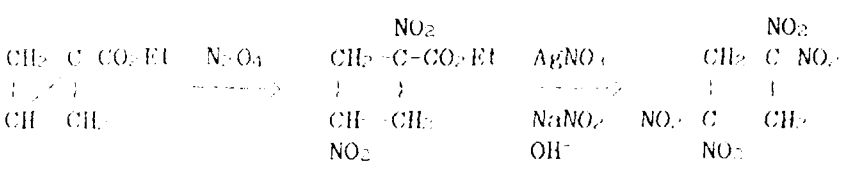
alternate route to this starting material more suitable to scale up than the literature method[9] was used. Allene cycloaddition with acrylonitrile[11] was used to prepare 3-methylenecyclobutane carbonitrile, and nitrile hydrolysis gave 3-methylenecyclobutanecarboxylic acid.[12] Subsequent esterification afforded ethyl 3-methylenecyclobutanecarboxylate.[9] Oxidative removal of the exo-methylene has been reported using either ozone[13] (87-90%) or osmium tetroxide/periodate (74%).[14]

Low temperature (0 °C) sodium borohydride reduction of the ketone gave ethyl 3-hydroxycyclobutane-1-carboxylate. Conversion of the alcohol to the bromide by tosylation and subsequent bromide displacement was reported.[9] Use of the mesylate instead of the tosylate resulted in improved reaction time (3 hours vs 2 days) and yield (94-99% overall vs 39-46%). Ethyl bicyclo[1.1.0]butane-1-carboxylate was prepared from the bromoester by the reported procedure[9], but the method *gave erratic results.* It was found that the addition of 5 mole-% of t-butyl alcohol led to an 85% isolated yield of ethyl bicyclo[1.1.0]butane-1-carboxylate.

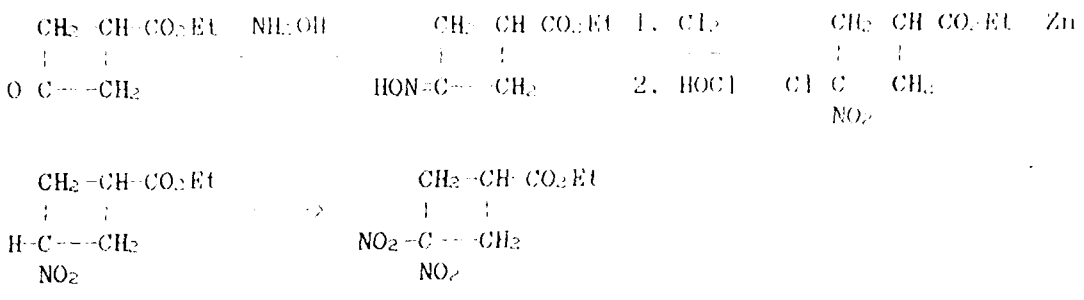


Reaction of ethyl bicyclo[1.1.0]butane-1-carboxylate with dinitrogen tetroxide by the procedure reported for another bicyclobutane derivative[12] produced ethyl 1,3-dinitrocyclobutane-1-carboxylate in 30-40% yield, as a

mixture of *cis/trans* isomers. One isomer was an oil, and the other was a solid which was recrystallized from ether-hexane after column chromatography. Oxidative nitration of the isomeric mixture at 5 °C in aqueous THF using Kaplan-Shechter conditions afforded TNCB in 10-22% yields. A total of 13.6 g of TNCB was prepared by this method. Using methyl bicyclo-[1.1.0]butane-1-carboxylate instead of the ethyl ester in this sequence resulted in lower yields in the N_2O_4 addition step.

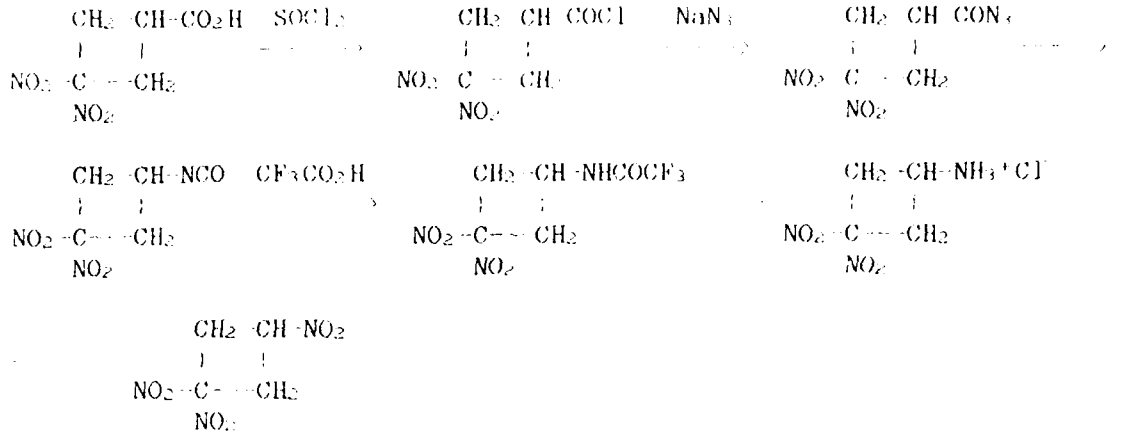


Another potential route to TNCB was investigated in which the key intermediate is ethyl 3-oxocyclobutane-1-carboxylate, described above. Oximination followed by reaction of the oxime with chlorine gas at 0 °C afforded the chloronitroso derivative. Subsequent hypochlorite oxidation gave ethyl 3-chloro-3-nitro-cyclobutanecarboxylate. Zinc-promoted dechlorination[15] gave ethyl 3-nitrocyclobutanecarboxylate in 73% yield. Oxidative nitration by the persulfate method proceeded in 33-50% yield to give ethyl 3,3-dinitrocyclobutane carboxylate. Ester hydrolysis gave the dinitro acid in 93% yield. Alternatively, oxidative nitration and concomitant ester hydrolysis was achieved in 47%-56% yield in a one-pot process. In a preliminary run, 3-oxocyclobutanecarboxylic acid was produced, but the use of a large excess of sodium nitrite avoided the formation of Nef product.



Treatment of 3,3-dinitrocyclobutanecarboxylic acid with thionyl chloride to give the acid chloride, followed by reaction with sodium azide under phase transfer conditions[16] and trifluoroacetolysis gave N-(3,3-dinitrocyclobutyl)trifluoroacetamide in 84% overall yield from dinitrocyclobutanecarboxylic acid. Diphenylphosphoryl azide[17] in alcohols, on the other hand, converted 3,3-dinitrocyclobutanecarboxylic acid (DNB-CO_2H) into mixtures of the carbamates (DNB-NH-CO_2R) and amide (DNB-NH-CO-DNB).

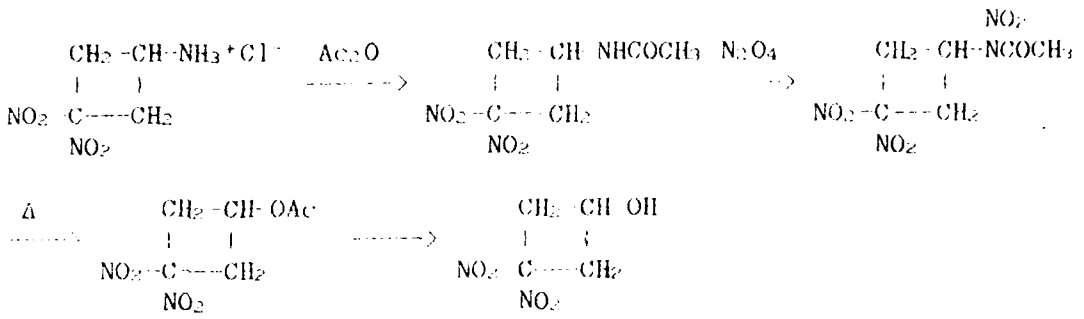
Methanolic hydrochloric acid hydrolyzed N-(3,3-dinitrocyclobutyl)-trifluoroacetamide quantitatively to 3,3-dinitrocyclobutylamine hydrochloride. The free amine was unstable, but reaction of the salt with m-CPBA following the procedure of Borden[18] gave impure 1,1,3-trinitrocyclobutane contaminated with m-chlorobenzoic acid. Crystallization and chromatographic techniques were ineffective in removing all the chlorobenzoic acid. Use of sodium bicarbonate as a buffer in the amine oxidation reaction resulted in decomposition.



Kaplan-Shechter oxidative nitration conditions used previously[1] with 1,3-dinitrocyclobutane led to decomposition of 1,1,3-trinitrocyclobutane. The use of sodium carbonate in place of sodium hydroxide in this reaction gave the same results. Methanolic tetranitromethane and sodium carbonate or phosphate, in the presence of excess sodium nitrite, gave recovered trinitro compound. Starting material was decomposed after a four day reaction period using sodium phosphate as a base.

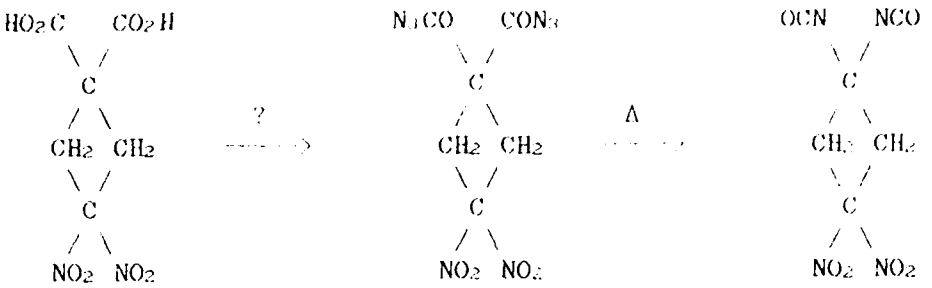
Another approach to TNCB is based on the nitration[19] reaction of the oxime of 3,3-dinitrocyclobutanone. Accordingly, 3,3-dinitrocyclobutylamine hydrochloride was acetylated with acetic anhydride (62%) and the amide was treated with dinitrogen tetroxide. Thermolytic nitrogen extrusion[20] from the intermediate N-(3,3-dinitrocyclobutyl)-N-nitrosoacetamide afforded 3-acetoxy-1,1-dinitrocyclobutane (90%). Acetate hydrolysis gave the alcohol.

3-Acetoxy-1,1-dinitrocyclobutane was also prepared, in 20% yield, from 3,3-dinitrocyclobutylamine hydrochloride via direct diazatization[21] using sodium nitrite in acetic acid. A by-product was the alcohol.



Attempts to oxidize this alcohol to 3,3-dinitrocyclobutanone were unsuccessful. Reagents employed included pyridinium chlorochromate[22], cerric ammonium nitrate[10] and chromic anhydride[23] using ether[24] or acetone[25] as a co-solvent. Oxidation of 3,3-dinitrocyclobutylamine hydrochloride was also investigated. No reaction took place under standard amine oxidation conditions using sodium tungstate[26], and reactions with N-chlorosuccinimide, sodium hypochloride[27] or N-methyl-4-formylpyridinium benzenesulfonate[28] followed by base treatment were also ineffective.

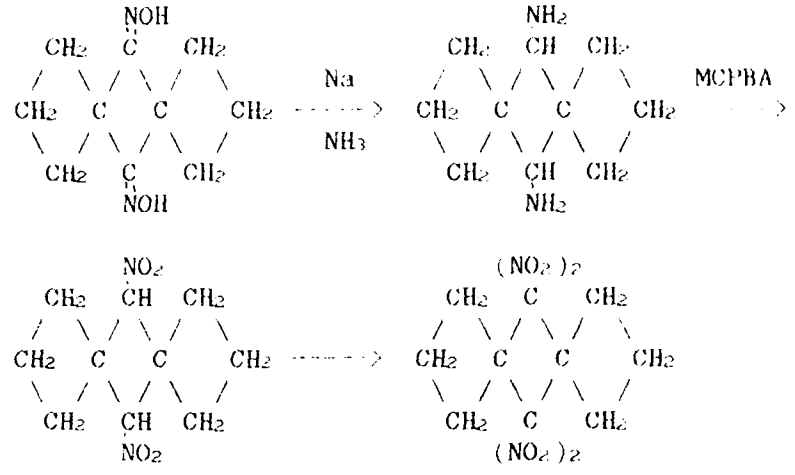
Another approach to cyclobutane structures is to condense 1,3-dihalo compounds with malonate derivatives. Accordingly, the reported synthesis of diethyl 3-oxocyclobutane-1,1-dicarboxylate[29] was repeated; condensation of diethyl malonate with 1-bromo-3-chloro-2-benzyloxypropane (71%) was followed by debenzylation and pyridinium chlorochromate oxidation (44%). Oximination (73%) followed by chloronitration afforded diethyl 3-chloro-3-nitrocyclobutane-1,1-dicarboxylate (74%). Reductive dechlorination (70%) and combined oxidative nitration and ester hydrolysis afforded 3,3-dinitrocyclobutane-1,1-dicarboxylic acid in 65% yield.



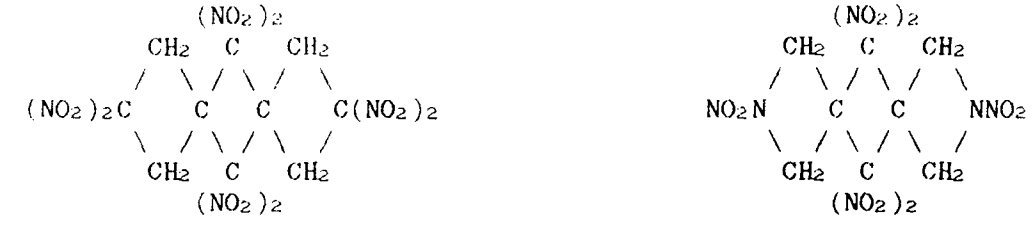
Conversion of this diacid to the ketone by Curtius rearrangement, followed by hydrolysis was contemplated. A thionyl chloride reaction failed to give the acid chloride, and partial loss of nitro groups was observed. Attempts to convert the diacid directly to the diacyl azide by the mixed carboxylic-carbonic anhydride method[30] were also unsuccessful.

Spiro Derivatives. The synthesis of compounds with two or more four-membered joined with a *spiro ring junction* is expected to provide improved explosive performance because of added ring strain. Another advantage of joined rings is that hydrogens removed by the ring junction result in increased oxygen balance.

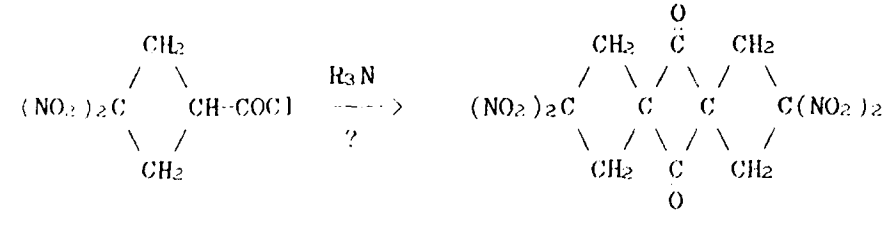
In the preceding report[1], the synthesis of the model compound, 5,5,10,10-tetranitrodispiro[3.1.3.1]decane from dispiro[3.1.3.1]decane-5,10-dione was described. The ketone was converted to its oxime, which was then reduced with sodium in liquid ammonia to give the diamine. Oxidation with m-chloroperbenzoic acid gave the 5,10-dinitro derivative and ferricyanide-persulfate oxidative nitration gave 5,5,10,10-tetranitrodispiro-[3.1.3.1]decane (mp 180 °C).



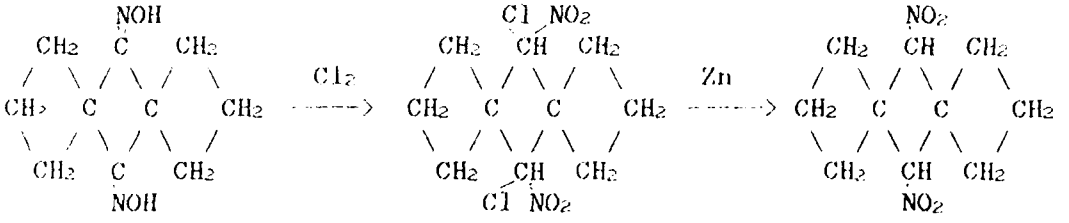
Target compounds with this skeletal structure for which synthesis routes are readily devised are 2,2,5,5,8,8,10,10-octanitrodispiro[3.1.3.1]decane and 2,8-dinitraza-5,5,10,10-tetranitrodispiro[3.1.3.1]decane.



Dispiro compounds of this type are generally accessible by the dimerization of ketenes obtained by the reaction of acid chlorides with amines. Starting materials for this route, 3,3-dinitrocyclobutane carboxylic acid and 1-nitro-3-carboxyazetidine[32], were prepared earlier on this program.

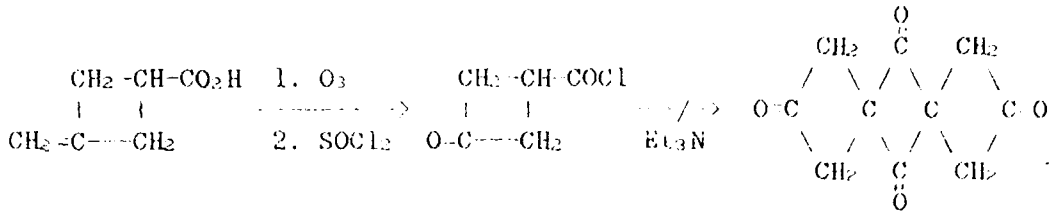


Because *gem*-dinitro groups would not survive the oxime reduction conditions employed in the model reaction, it was shown that oxime halogenation route can be used in this type of structure. Reaction of 5,10-dioximinodispiro[3.1.3.1]decane with chlorine gave the corresponding bis chloronitroso derivative following a standard procedure. Aqueous sodium hypochlorite oxidation gave an isomeric mixture of 5,10-dichloro-5,10-dinitro-dispiro[3.1.3.1]decanes in near quantitative yield. Zinc induced reductive dechlorination gave 5,10-dinitrodispiro[3.1.3.1]decane.



3,3-Dinitrocyclobutanecarboxylic acid was converted to the acid chloride using thionyl chloride. This acid chloride, however, gave polymeric material under ketene dimerization conditions,[31] and the tetranitrodispirane was not obtained. Similar results were obtained using 1-nitro-3-carboxy-azetidine,[32] as well as 3-chloro-3-nitrocyclobutanecarboxylic acid chloride.

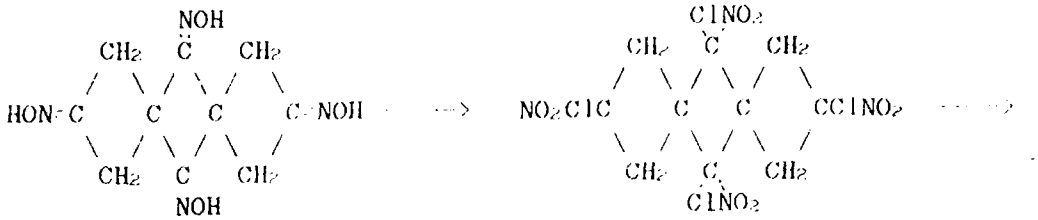
Since a high efficiency conversion of the model oxime to the *gem*-dinitro derivative was demonstrated, the synthesis of 2,5,8,10-tetraoximino-dispiro[3.1.3.1]decane was undertaken. 3-Methylenecyclobutanecarboxylic acid was ozonized to give 3-oxocyclobutanecarboxylic acid, which was converted to 3-oxocyclobutanecarboxylic acid chloride in 65% overall yield. However, reaction of this acid chloride with triethylamine afforded only polymer and no tetraoxodispiro[3.1.3.1]decane.

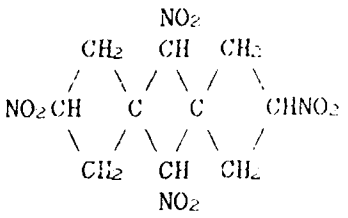


Subsequently, 3-benzyloxycyclobutanecarboxylic acid[9] was converted to the acid chloride and reaction with triethylamine afforded 2,8-bis-(benzyloxy)-5,10-dioxodispiro[3.1.3.1]decane in 41-48% yield. Reductive debenzylation did not occur at 20 °C under the usual hydrogenolysis conditions (4 atm, $Pd(OH)_2$), but at 50-53 °C a quantitative yield of 2,8-dihydroxy-5,10-dioxodispiro[3.1.3.1]decane was realized. However, attempts to oxidize this diol to the ketone using pyridinium chlorochromate[22] or oxalyl chloride[33] were unsuccessful.

3-Methylenecyclobutanecarboxylic acid chloride[13] was prepared from the corresponding acid. *In-situ* ketene generation and dimerization afforded 2,8-dimethylene-5,10-dioxodispiro[3.1.3.1]decane (50%) which, after ozonolysis, gave the desired tetraketone (55%) Exhaustive oximination gave 2,5,8,10-tetraoximinodispiro[3.1.3.1]decane (56%). Attempts to reduce the tetraoxime to the tetramine using sodium in ammonia,[34] lithium aluminum hydride[35] or catalytic hydrogenation failed.

2,5,8,10-Tetraoximinodispiro[3.1.3.1]decane was chloronitrated to afford an isomeric mixture of 2,5,8,10-tetrachloro-2,5,8,10-tetranitrodispiro[3.1.3.1]-decanes. Reductive dechlorination gave a 20% yield of 2,5,8,10-tetranitrodispiro[3.1.3.1]decane.





B. Experimental

Melting points are uncorrected. Elemental analysis was performed by Galbraith Laboratories, Knoxville, TN. NMR spectra were recorded on a Varian T-60 spectrometer. Infrared spectra were recorded with a Perkin-Elmer 700 spectrometer.

3-Methylenecyclobutanecarboxylic Acid. The procedure of Cripps, Williams and Sharkey[13] was modified as follows: A solution of 3-methylenecyclobutanecarbonitrile (54.5 g, 0.585 mol) and sodium hydroxide (46.8 g, 1.17 mol) in 225 mL of water was refluxed for 20 h, and cooled to 15 °C. Saturated aqueous sodium chloride solution (200 mL) was added and the solution was acidified to pH 1 with concentrated hydrochloric acid (125 mL). The aqueous layer was extracted with ether (4 x 200 mL) and the organic phases were combined, dried ($MgSO_4$) and concentrated. Distillation through a 4 inch Vigreux-shortpath afforded 63.0 g (96%) of 3-methylenecyclobutanecarboxylic acid: bp 79-80 °C(0.4 mm). (lit[13] bp 119 °C (26 mm)). *IR* (CH_2Cl_2) 3000, 1750, 1700, 1405, 1200 cm^{-1}.

Ethyl 3-Methylenecyclobutanecarboxylate. The procedure of Gajewski and Burka[36] was modified as follows: A solution of 3-methylenecyclobutane-

carboxylic acid (159.0 g, 1.418 mol) and concentrated sulfuric acid (0.60 g, 6.1 mmol) in 700 mL of 1:1 absolute ethanol-benzene was refluxed for 24 h and concentrated by distillation through a 12 " Vigreux column. Ether (500 mL) was added and the organic phase washed with 1 M aqueous sodium carbonate solution (100 mL). The aqueous phase was extracted with ether and the combined organic layers were dried ($MgSO_4$) and concentrated. Distillation of the residue from a large flask (500 mL, foaming!) through a 6" vacuum jacketed Vigreux column gave 188 g (94%) of ethyl 3-methylenecyclobutanecarboxylate: bp 78-79 °C (26 mm). IR and NMR were in accord with previously published data.[36]

Ethyl 3-Oxocyclobutanecarboxylate. Ozone generated with a Welsbach Ozonator (T-23) was passed through a solution of ethyl 3-methylenecyclobutanecarboxylate (100 g, 0.714 mol) in 700 mL of methanol until the blue color of dissolved ozone persisted (*ca. 7 h required*). Dimethyl sulfide (100 mL) was added slowly and the dry ice bath was allowed to warm gradually to room temperature. The organic phase was stirred overnight and concentrated. Methylene chloride (600 mL) was added and the mixture was washed with water (4 x 200 mL), dried ($MgSO_4$), concentrated and distilled through a 4" Vigreux to afford 91.7 g (90%) of ethyl 3-oxocyclobutanecarboxylate: bp 68-70 °C (.5 mm); lit[13] bp 90 °C (2 mm); IR (CH_2Cl_2) 3030, 1790, 1730 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.33 (t, 3 H, J = 7 Hz), $-OCH_2CH_3$), 3.33 (br s, 5 H, $-CH_2-$), 4.18 (q, 2 H, J = 7 Hz, $-OCH_2CH_3$)

Ethyl 3-Chloro-3-nitrocyclobutanecarboxylate. A slow stream of chlorine gas was bubbled into a stirred solution of ethyl 3-oximinocyclobutanecarboxylate (8.00 g, 50.9 mmol) in 50 mL of methylene chloride at 0 °C until the initially blue solution became greenish. Excess chlorine and

solvent were removed by rotary evaporation and then 100 mL of benzene, 100 mL of pH 10.5 bleach (5.0% sodium hypochlorite) and tetrabutylammonium hydrogen sulfate (5.0 g, 15 mmol) were added. The resulting two-phase mixture was stirred briskly while it was cooled in a 10 °C bath. After 1 h, the phases were separated and the aqueous layer extracted with ether (2 x 50 mL) and the combined organic layers were washed with saturated sodium chloride solution, dried ($MgSO_4$) and concentrated. Distillation afforded 9.45 g (89%) of ethyl 3-chloro-3-nitrocyclobutanecarboxylate as a mixture of isomers: bp 72-74 °C (0.3 mm); IR (CH_2Cl_2) 17.30; 1550 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.40 (t, 3 H, J = 7 Hz); 3.35 (m, 5 H), 4.20 (q, 2 H, J = 7 Hz).

Anal. Calcd for $C_7H_{10}ClNO_4$: C, 40.50; H, 4.86; Cl, 17.08; N, 6.75. Found: C, 40.50; H, 5.41; Cl, 17.40; N, 6.62.

A larger run conducted with 110 g (0.700 mol) of ethyl 3-oximinocyclobutanecarboxylate and chlorine gas in 1 L of methylene chloride followed by nitroso oxidation using 2 L of 5% bleach and 78 g of tetrabutylammonium hydrogen sulfate in 1 L of benzene afforded 124 g (86%) of ethyl 3-chloro-3-nitrocyclobutanecarboxylate after workup and distillation:

Ethyl 3-Nitrocyclobutanecarboxylate. To a solution of ethyl 3-chloro-3-nitrocyclobutanecarboxylate (5.00 g, 24 mmol) in 100 mL of tetrahydrofuran was added a solution of hydroxylamine hydrochloride (1.80 g , 25 mmol) in 15 mL of water. Zinc dust (2.00 g, 30.6 mmol) was added portionwise with stirring over a 10 min period at 25 °C. A cooling bath was used. After 1 h, 100 mL of water was added and the mixture extracted twice with ether. The combined organic layers were washed with saturated

sodium chloride solution, dried ($MgSO_4$) and concentrated. Short-path distillation afforded 3.38 g (80%) of ethyl 3-nitrocyclobutanecarboxylate.

An analytical sample was obtained by dispersing 1 g of the material in 10 mL of ice cold M aqueous sodium hydroxide solution. After the mixture was stirred vigorously for 1 h, it was extracted with methylene chloride (3 x 10 mL), and then carefully acidified to pH 5 with glacial acetic acid. The product was extracted with methylene chloride (2 x 20 mL) and the combined organic phases washed with 1 M aqueous sodium bicarbonate solution and saturated sodium chloride solution. The organic phase was dried ($MgSO_4$) and concentrated, and the residue was distilled to give an isomeric mixture of ethyl 3-nitrocyclobutanecarboxylate: bp 84-87 °C (0.1 mm); IR (CH_2Cl_2) 3050, 1735, 1550 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.25 (t, 3 H, J = 7 Hz), 2,80 (m, 3 H), 3.05 (m, 2 H), 4.05 (q, 2 H, J = 7 Hz), 4.85 (m, 1 H).

Anal. Calcd for $C_7H_{11}NO_4$: C, 48.55, H, 6.40, N, 8.09. Found: C, 48.17; H, 5.88; N, 7.41.

Ethyl 3,3-Dinitrocyclobutanecarboxylate. A solution of potassium t-butoxide (4.57 g, 40.8 mmol) in 50 mL of tetrahydrofuran and 25 ml of ethanol was stirred at 25 °C for 5 min before ethyl 3-nitrocyclobutanecarboxylate (5.66 g, 32.6 mmol) was added dropwise. A 20 °C water bath was used to moderate the reaction temperature. After 5 min, a solution of sodium nitrite (28.3 g, 0.41 mol) in 50 mL of water was added followed immediately by a solution of sodium persulfate (18.6 g, 78.1 mmol) and potassium ferricyanide (5.70 g, 17.3 mmol) in 100 mL of water. After the solution was stirred for 1 h, it was extracted with ether (3 x 50 mL), and the combined organic layers were washed with saturated sodium chloride

solution, dried ($MgSO_4$) and concentrated. Short-path distillation afforded 3.87 g (54%) of ethyl 3,3-dinitrocyclobutanecarboxylate: bp 100–103 °C (0.2 mm); IR (CH_2Cl_2) 3050, 1735, 1560, 1335 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.35 (t, 3 H, J = 7 Hz), 3.37 (br s, 5 H), 4.15 (q, 2 H, J = 7 Hz). An analytical sample was obtained by distillation through a 4" Vigreux column to give a fraction boiling at 102 °C (0.2 mm).

Anal. Calcd for $C_7H_{10}N_2O_6$: C, 38.54; H, 4.62; N, 12.84. Found: C, 38.52; H, 4.83; N, 12.17.

3,3-Dinitrocyclobutanecarboxylic Acid. A solution of ethyl 3,3-dinitrocyclobutanecarboxylate (1.10 g, 5.04 mmol) and sodium hydroxide (0.30 g, 7.5 mmol) in 16 mL of ethanol and 4 mL of water was refluxed for 1 h, cooled to 5 °C and acidified with 10% aqueous hydrochloric acid. The combined organic layers were extracted with ether (3 x 25 mL), washed with saturated sodium chloride solution, dried ($MgSO_4$) and concentrated to give 0.89 g (93%) of crystalline solid. Recrystalliation from ether–hexanes afforded an analytical sample: mp 96–97 °C; IR (CH_2Cl_2) 3050, 1710, 1560 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.43 (br s, 5 H), 10.2 (s, 1 H, D_2O exch.).

Anal. Calcd for $C_5H_6N_2O_6$: C, 31.59; H, 3.18; N, 14.73. Found: C,31.52; H, 3.13; N, 14.12.

3,3-Dinitrocyclobutanecarboxylic acid was also prepared from ethyl 3-nitrocyclobutanecarboxylate. A 0 °C solution of sodium hydroxide (0.60 g, 15 mmol) and ethyl 3-nitrocyclobutanecarboxylate (1.00 g, 5.77 mmol) in 12 mL of 3:1 water–tetrahydrofuran was stirred briskly for 30 min before sodium nitrite (2.0 g, 29 mmol) was added. After 5 min, this solution was poured into a freshly prepared solution of sodium persulfate (3.30 g, 13.8 mmol) and potassium ferricyanide (1.00 g, 3.04 mmol) in 25 mL of water at

25 °C. A 10 °C water bath was used. After 1 h, methylene chloride was added (50 mL) and sufficient ice-cold hydrochloric acid (6 M) to give a pH 2-3 solution. The phases were separated and the aqueous phase was extracted with methylene chloride (2 x 25 mL). The combined organic layers were washed with saturated sodium chloride solution, dried ($MgSO_4$) and concentrated to afford 0.987 g of semi-crystalline solid. Two triturations with 3:1 hexane/methylene chloride afforded 0.62 g (56%) of 3,3-dinitrocyclobutanecarboxylic acid: mp 90-94 °C. Recrystallization from ether-hexanes afforded an analytical sample: mp 96-97 °C; IR (CH_2Cl_2) 3050, 1710, 1560 cm-1; 1H NMR ($CDCl_3$) δ 3.43 (br s, 5 H), 10.2 (s, 1 H, D_2O exch.).

Anal. Calcd for $C_5H_6N_2O_6$: C, 31.59; H, 3.18; N, 14.73. Found: C, 31.52; H, 3.13; N, 14.12.

Ethyl N-(3,3-Dinitrocyclobutyl)carbamate and N-(3,3-Dinitrocyclobutyl)-3,3-dinitrocyclobutanecarboxamide. A solution of 3,3-dinitrocyclobutane-1-carboxylic acid, (0.50 g, 2.63 mmol), triethylamine (0.280 g, 2.77 mmol) and diphenylphosphoryl azide (0.760 g, 2.76 mmol) in 5 mL of dioxane containing absolute ethanol (0.20 g, 4.3 mmol) was refluxed for 20 h. The solution was diluted with ether and washed with dilute ice-cold hydrochloric acid solution. The separated aqueous phase was extracted with ether (2 x 20 mL) and the combined organic phases were washed with 1 M sodium carbonate solution, dried ($MgSO_4$) and concentrated to give a solid. Trituration twice with 1:1 hexane-ether afforded 100 mg (23%) of N-(3,3-dinitrocyclobutyl)-3,3-dinitrocyclobutanecarboxamide: mp 236-237 °C; IR (KBr) 3420, 1655, 1550, 1350, 1270 cm^{-1}; 1H NMR (d_6-acetone) δ 3.40 (br s,

4 H, $-CH_2-$), 3.50 (br s, 4 H, $-CH_2-$), 4.28 (pent, 2 H, J = 7 Hz, -CH-), 6.20 (br s, 1 H, NH).

Anal. Calcd for $C_9H_{11}N_5O_6$: C, 32.44; H, 3.33; N, 21.02. Found: C, 32.35; H, 3.97; N, 20.96.

The above filtrates were concentrated to afford 0.39 g (64%) of ethyl N-(3,3-dinitrocyclobutyl)carbamate. An analytical sample was obtained by recrystallization from ether-hexanes: mp 86-87 °C; IR (CH_2Cl_2) 3650, 3500, 3020, 1720, 1560, 1420, 1330 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.35 (t, 3 H, J = 7 Hz, CH_3-), 3.38 (m, 4 H, $-CH_2-$), 4.10 (q, 2 H, J = 7 Hz, $-CH_2-$), 4.12 (m, 1 H, -CH-), 5.50 (br s, 1 H, NH).

Anal. Calcd for $C_7H_{11}N_3O_6$: C, 36.06; H, 4.76; N, 18.02. Found: C, 35.77; H, 4.68; N, 17.75.

N-(3,3-Dinitrocyclobutyl)trifluoroacetamide. A solution of 3,3-dinitrocyclobutane-1-carboxylic acid (10.00 g, 52.6 mmol) in 30 mL of thionyl chloride was stirred at room temperature for 24 h before the excess thionyl chloride was removed by rotary evaporation. Methylene chloride (100 mL) was introduced, the solution was cooled to 0 °C and tetrabutylammonium chloride (150 mg, 0.54 mmol) and a solution of sodium azide (4.50 g, 69.2 mmol) in 15 mL of water were added. The two-phase mixture was stirred briskly for 3 h at 0 °C, the phases were separated and the organic layer was washed with water (2 x 25 mL) and dried ($MgSO_4$). IR (CH_2Cl_2) indicated bands at 2190, 1715, 1565, 1420, 1360 and 1340 cm^{-1} for the acyl azide. The solution was filtered and refluxed for 18 h after addition of trifluoroacetic acid (8.0 g, 70 mmol). The cooled mixture was washed with ice-cold 1 M sodium bicarbonate solution (25 mL), dried ($MgSO_4$) and concentrated to afford a yellow solid. Ether was added (100 mL) and the

mixture filtered to remove a small amount of ether-insoluble impurity. The filtrate was concentrated to afford 11.3 g (84%) of N-(3,3-dinitrocyclobutyl)trifluoroacetamide: mp 82-84 °C; TLC (ether) R_f = 0.10; IR (CH_2Cl_2) 3480, 3100, 1730, 1560, 1335, 1220, 1170 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.50 (m, 4 H, $-CH_2-$), 4.52 (m, 1 H), 7.0 (br s, 1 H, NH).

Anal. Calcd for $C_6H_6F_3N_3O_5$: C, 28.03; H, 2.35; N, 16.34; F, 22.16. Found: C, 28.01; H, 2.86; N, 16.38; F, 22.14.

3,3-Dinitrocyclobutylamine Hydrochloride. To a solution of N-(3,3-dinitrocyclobutyl)trifluoroacetamide (11.3 g, 44.0 mmol) in 200 mL of methanol was added 20 mL of 12 M hydrochloric acid. The solution was refluxed overnight and volatiles were removed using a rotary evaporator. Two ether triturations afforded 8.70 g (100%) of 3,3-dinitrocyclobutylamine hydrochloride: mp 215-217 °C (decomp); IR (KBr) 3000, 1560, 1345 cm^{-1}; ^1H NMR (d_6-DMSO/$CDCl_3$) δ 3.60 (m, 5 H, $-CH_2-$), 8.50 (br s, 3 H, $-NH_3$).

Anal. Calcd for $C_4H_8N_3ClO_4$: C, 24.32; H, 4.08; N, 21.27; Cl, 17.94. Found: C, 24.70; H, 4.26; N, 21.31; Cl, 17.56.

N-(3,3-Dinitrocyclobutyl)acetamide. A mixture of 3,3-dinitrocyclobutylamine hydrochloride (0.50 g, 2.53 mmol), anhydrous sodium acetate (0.25 g, 3.0 mmol) and 1 mL of acetic anhydride in 5 mL of glacial acetic acid was stirred for 24 h at room temperature. The solution was poured into water and methylene chloride, the phases separated and the organic layer washed successively with water (10 mL) and 1 M sodium carbonate (2 x 20 mL) dried ($MgSO_4$) and concentrated to afford 0.32 g (62%) of N-(3,3-dinitrocyclobutyl)acetamide. Two triturations with cold ether afforded the analytical sample: mp 115-116 °C; TLC (ether) R_f = 0.32; IR ($CHCl_2$) 3500,

1680, 1560, 1365 cm^{-1}; ^1H NMR ($CDCl_3$-d_6 acetone) δ 1.92 (s, 3 H), 3.40 (br d, 4 H), 4.40 (pent, 1 H), 7.409 (br s, NH).

Anal. Calcd for $C_6H_9N_3O_5$: C, 35.47; H, 4.47; N, 20.68.Found: C, 35.35; H, 4.59; N, 20.16.

N-(3,3-Dinitrocyclobutyl)-N-nitrosoacetamide. Under argon, a solution of dinitrogen tetroxide (0.52 g, 5.6 mmol) in 10 mL of methylene chloride was chilled to -70 °C using a dry ice bath. Anhydrous sodium acetate (0.93 g, 11.3 mmol) was added portionwise. The mixture was warmed to 0 °C by replacing the dry ice bath with an ice-water bath and N-(3,3-dinitrocyclobutyl)acetamide (0.76 g, 3.7 mmol) was added. The solution was stirred for 20 min and then poured onto ice and water. The aqueous layer was extracted with cold methylene chloride (3 x 25 mL), and the organic phases were dried ($MgSO_4$) and concentrated. The resulting yellow solid (1.3 g) was triturated twice with hexane and dried in vacuo to give N-(3,3-dinitrocyclobutyl)-N-nitrosoacetamide (0.81 g, 93 %): mp 86 °C (decomp); IR (CH_2Cl_2) 1740, 1575, 1540 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.70 (s, 3 H). 3.40 (m, 4 H), 5.18 (d, 1 H).

Anal. Calcd for $C_6H_8N_4O_6$: C, 31.04, H, 3.47; N, 21.13. Found: C, 31.18; H, 3.39; N, 23.65.

1,1-Dinitro-3-acetoxycyclobutane. A solution of N-(3,3-dinitrocyclobutyl)-N-nitrosoacetamide (0.78 g, 3.36 mmol) in 50 mL of hexanes was refluxed for 22 h, filtered, dried and concentrated to give 0.62 g (90%) of 1,1-dinitro-3-acetoxycyclobutane: IR (CH_2Cl_2) 1740, 1565 cm.$^{-1}$ ^1H NMR ($CDCl_3$) δ 2.0 (s, 3 H), 3.40 (m, 4 H), 5.0 (pent, 1 H, J = 7 Hz).

Diethyl 3-Chloro-3-nitrocyclobutane-1,1-dicarboxylate. To a 0 °C solution of diethyl 3-oximinocyclobutane-1,1-dicarboxylate (22.8 g, 99.5

mmol) in 150 mL of methylene chloride was added chlorine gas until a persistent dark green coloration was observed. The solution was concentrated on a rotary evaporator and 200 mL of benzene, tetrabutylammonium hydrogen sulfate (10.0 g, 29 mmol) and 300 mL of bleach (5.2% sodium hypochlorite) were added successively. A cooling bath was used to moderate the slightly exothermic reaction. After the two phase solution was stirred briskly for 2 h, the separated aqueous layer was extracted with ether (2 x 100 mL) and the combined organic layers washed with saturated sodium chloride solution, dried ($MgSO_4$) and concentrated. Distillation gave 20.8 g (75%) of diethyl 3-chloro-3-nitrocyclobutane-1,1-dicarboxylate: bp 105-110 °C (0.2 mm); IR (CH_2Cl_2) 3650, 3080, 3030, 1725, 1560 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.35 (t, 6 H, J = 7 Hz), 3.40 (AB quartet, 4 H), 4.35 (q, J = 7 Hz).

Anal. Calcd for $C_{10}H_{14}ClNO_6$: C, 42.95; H, 5.05; N, 5.00; Cl, 12.67. Found: C, 43.13; H, 5.15; N, 4.32; Cl, 11.89.

3,3-Dinitrocyclobutane-1,1-dicarboxylic Acid. Hydroxylamine hydrochloride (5.60 g, 82 mmol) was added to a solution of diethyl 3-chloro-3-nitrocyclobutane-1,1-dicarboxylate (20.8 g, 74.4 mmol) in 200 mL of tetrahydrofuran and 50 mL of water. Zinc powder (6.30 g, 96.3 mmol) was then added portionwise, with cooling and stirring, over a 20 min period, and stirring was continued for 1 h. The mixture was diluted with water (200 mL) and extracted with ether (3 x 100 mL). The combined organic layers were washed with saturated sodium chloride solution, dried ($MgSO_4$) and concentrated. The residue was distilled to afford 14.2 g (78%) of diethyl 3-nitrocyclobutane-1,1-dicarboxylate: bp 110 °C (0.1 mm); IR(CH_2Cl_2) 1730,

1540 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.25 (t, 6 H, J = 7 Hz); 3.20 (d, 4 H, J = 7 Hz), 4.35 (q, 4 H, J = 7 Hz), 5.05 (pent, 1 H, J = 7 Hz).

The above nitrodiester (14.2 g, 57.9 mmol) was added to a solution of sodium hydroxide (9.50 g, 0.237 mol) in 240 mL of 3:1 water-tetrahydrofuran cooled to 0 °C. Brisk stirring was maintained until a homogeneous solution was obtained (20 min). Sodium nitrite (35 g, 0.51 mol) was added and stirring continued for 10 min. The solution was poured into a freshly prepared solution of sodium persulfate (35 g, 0.147 mol), potassium ferricyanide (9.50 g, 28.8 mmol) and sodium carbonate monohydrate (7.0 g, 56.4 mmol) in 175 mL of water. After the solution was stirred for 1 h at 22–25 °C, it was acidified to pH 2 with cold 6 M aqueous hydrochloride acid. The aqueous layer was extracted with methylene chloride (3 x 100 mL). The combined organic layers were washed with saturated sodium chloride solution, dried ($MgSO_4$) and concentrated and triturated with hexane to afford 7.06 g (52%) of 3,3-dinitrocyclobutane-1,1-dicarboxylic acid: mp 179–180 °C (decomp); IR (KBr) 3050, 1710, 1580, 1375, 1280, 1140 cm^{-1}; ^1H NMR (d_6-DMSO/$CDCl_3$) δ 3.55 (s, 4 H), 8.60 (br s, 1 H, $CO_2\underline{H}$).

Anal. Calcd for $C_6H_6N_2O_8$: C, 30.78; H, 2.58; N, 11.96. Found: C, 31.05; H, 2.86; N, 10.92.

Ethyl 3-Hydroxycyclobutane-1-carboxylate. To a 0 °C solution of ethyl 3-oxocyclobutane-1-carboxylate (24.8 g, 0.175 mol) in 175 mL ethanol, maintained at 0–3 °C, was added dropwise a solution of sodium borohydride (2.31 g, 87.5 mmol) in 25 mL of ethanol. After 30 min, glacial acetic acid was added dropwise until the excess hydride was decomposed. Water (250 mL) was added and the solution extracted with methylene chloride (3 x 125 mL). The combined organic layers were washed with 1 M sodium bicar-

bonate solution (100 mL), dried ($MgSO_4$) and concentrated. Short-path distillation at reduced pressure afforded 19.5 g (77%) of ethyl 3-hydroxycyclobutane-1-carboxylate: bp 94-98 °C (2 mm). (Lit[9,29] bp 130-135 °C (20 mm)); IR (CH_2Cl_2) 3650, 3530, 3010, 1720 cm^{-1}.

Ethyl 3-Bromocyclobutane-1-carboxylate. To a stirred solution of ethyl 3-hydroxycyclobutanecarboxylate (5.00 g, 34.7 mmol) and triethylamine (7.0 g, 69 mmol) in 50 mL of methylene chloride was added, dropwise, methanesulfonyl chloride (7.5 g, 65 mmol) while the temperature was maintained at -20 °C to -15 °C. The stirred suspension was allowed to warm to room temperature over a one hour period. The mixture was washed with cold dilute aqueous hydrochloric acid and 1 M aqueous sodium bicarbonate. The solution was dried ($MgSO_4$) and concentrated. Anhydrous lithium bromide (6.9 g, 80 mmol) and anhydrous acetone (25 mL) were added and the mixture was refluxed for 48 h. The cooled mixture was diluted with ether (50 mL) and washed with 1 M sodium bicarbonate solution, dried ($MgSO_4$) and concentrated. Short-path distillation afforded 6.25 g (87%) of ethyl 3-bromocyclobutanecarboxylate: bp 54-56 °C (0.6 mm).[9]

Ethyl Bicyclo[1.1.0]butane-1-carboxylate. A suspension of 60% sodium hydride (5.40 g 0.135 mole), *t*-butylcatechol (3-4 mg), *t*-butyl alcohol (0.36 g, 4.8 mmol) and ethyl 3-bromocyclobutane-1-carboxylate (20 g, 96.6 mmol) in 175 mL of anhydrous ether was protected from light and stirred for 4 days under an argon atomsphere. The solution was filtered and concentrated at 25 °C, and the residue was distilled to afford 10.4 g (85%) of ethyl bicyclo[1.1.0]butane-1-carboxylate: bp 45 °C(5 mm). The IR and NMR were as reported.[9] The product may be stored indefinitely at -78 °C, under

argon, in the presence of trace *t*-butycatechol. A run conducted with 104 g of bromoester afforded 54.0 g (85%) of ethyl bicyclobutanecarboxylate.

Ethyl 1,3-Dinitrocyclobutane-1-carboxylate. A solution of ethyl bicyclo[1.1.0]butane-1-carboxylate[9] (2.47 g, 19.6 mmol) in 35 mL of anhydrous ether was chilled to -20 °C and 6.4 mL (22 mmol) of a solution of dinitrogen tetroxide (3.11 g, 33.8 mmol) in 10 mL of ether was added dropwise. The resulting yellow-green solution was stirred for 10 min at -20 °C and 25 mL of absolute ethanol was added. The mixture allowed to warm to room temperature overnight. Solvent was removed and the residue was chromatographed on silica gel (30 g) using 3:1 hexane-ether to afford 1.73 g (40%) of ethyl 1,3-dinitrocyclobutane-1-carboxylate as a mixture of isomers. One of these isomers could be crystallized from the mixture using ether-hexane. This white solid (0.30 g, 7%) had R_f = 0.20 (2:1 hexane- ether); mp 87-89 °C; IR (CH_2Cl_2) *1750, 1550, 1370 cm*$^{-1}$; ^{1}H NMR ($CDCl_3$) $\underline{S}$ 1.33 (t, 3 H, J = 7 Hz), 3.42 (m, 4 H, $-CH_2-$), 4.27 (q, 2 H, J = 7 Hz), 4.93 (m, 1 H, $-CHNO_2$).

Anal. Calcd for $C_7H_{10}N_2O_6$: C, 38.54; 4.62; N, 12.84. Found: C, 38.39; H, 4.99; N, 12.63.

Methyl 1,3-Dinitrocyclobutane-1-carboxylate. To a solution of methyl bicyclo[1.1.0]butane-1-carboxylate (16.5 g, 0.147 mol) in 300 mL of anhydrous ether at -20 °C was added dropwise a solution of dinitrogen tetroxide (15.0 g, 0.16 mol) in 50 mL of cold (-30 °C) ether. A dry-ice acetone bath was used to maintain the solution temp between -20 °C and -15 °C. After an additional 10 min at -20 °C, methanol (50 mL) was added and the reaction allowed to warm to room temperature overnight. Solvent was evaporated and the residue was chromatographed (100 g of silica gel, 3:1

hexane ether) to afford 5.10 g (17%) of methyl 1,3-dinitrocyclobutane-1-carboxylate as a mixture of isomers. One of these isomers was obtained in crystalline form from ether-hexane: mp 38-40 °C; TLC (2:1 hexane-ether) R_f = 0.24 ; IR (CH_2Cl_2) 1750, 1550, 1365 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.56 (d, 2 J, J = 7 Hz, $-CH_2-$), 3.60 (d, 2 H, J = 2 Hz, $-CH_2-$), 3.96 (s, 3 H, CO_2CH_3), 5.03 (d pent, 1 H, J = 2 Hz, $-CHNO_2$).

Anal. Calcd for $C_6H_8N_2O_6$: C, 35.30; H, 3.95; N, 13.72. Found: C, 35.63; H, 4.01; N, 13.39.

1,1,3,3-Tetranitrocyclobutane. To a stirred solution of ethyl 1,3-dinitrocyclobutane-1-carboxylate in 100 mL of water and 40 mL of tetrahydrofuran at 0 °C was added sodium hydroxide (2.70 g, 67.5 mmol). After 15 min, sodium nitrite (7.7 g, 0.11 mol) was added and stirring was continued for an additional 5 min period. Ether (100 mL) and a solution of silver nitrate (19.0 g, 0.112 mol) in 100 mL of water were added and the resulting mixture was stirred briskly for 1 h at 0 °C. The ice bath was removed and stirring was continued an additional 2 h. Aqueous saturated sodium chloride (50 mL) was added, the suspension filtered and the aqueous layer extracted with ether (3 x 50 mL). The combined organic layers were washed with saturated sodium chloride solution, dried ($MgSO_4$) and concentrated to give a semi-solid. Trituration with ether-hexanes and washing with cold anhydrous ether afforded 0.61 g (11%) of 1,1,3,3-tetranitrocyclobutane: mp 165-166 °C. The filtrates were combined and concentrated. Repetition of the trituration procedures afforded an additional 0.53 g (10%) of product: mp 164-165 °C. IR (CH_2Cl_2) 3000, 1595, 1400, 1365, 1330 cm^{-1}; ^1H NMR (d_6-acetone) δ 4.73 (s).

Anal. Calcd for $C_4H_4N_4N_4O_8$: C, 20.35; H, 1.71; N, 23.73. Found: C, 20.47; H, 1.78; N, 22.25, 21.93

3-Benzyloxycyclobutanecarboxylic Acid. The following procedure is a modification of that of Wiberg[9]. Diethylmalonate (2250 g, 14.1 mol) was added with stirring to a solution of potassium t-butoxide (1163 g, 10.4 mol) in 12.5 L of dimethyl sulfoxide. After 15 min, 2-benzyloxy-1-bromo-3-chloropropane[29] (1237 g, 4.70 mol) was added slowly and the mixture was heated at 120 °C for 21 h. The solution was cooled to room temperature, diluted with 15 L of water and extracted with ether (3 x 5 L). The combined organic layers were washed with water (3 x 4 L) and with saturated sodium chloride solution (3 L), dried ($MgSO_4$) and concentrated. Distillation through a large short-path distillation apparatus gave a forerun (bp 60-115 °C (15mm)) followed by 716 g (50%) of diethyl 3-benzyloxycyclobutane-1,1-dicarboxylate: bp 165-190 °C (0.4 mm). To a solution of the diester (716 g) in 1 L of ethanol was added a solution of 85% potassium hydroxide (620 g, 9.38 mol) in 350 mL of water. This mixture was stirred and refluxed for 2 h, cooled, acidified to pH 1-2 with cold concentrated aqueous hydrochloric acid and extracted with ether (4 x 500 mL). The combined organic phases were washed with water, dried ($MgSO_4$) and concentrated to afford a yellow solid. This diacid was heated at ca. 200 °C under reflux condenser until CO_2 evolution ceased. The product was distilled through a one inch vigroux to afford 357 g (74%) of 3-benzyloxycyclobutanecarboxylic acid: bp 195-202 °C (2-3mm). Lit[9,29] bp 146-150 °C (0.1 mm).

3-Benzyloxycyclobutanecarboxylic Acid Chloride. A solution of 3-benzyloxycyclobutanecarboxylic acid (10.0 g, 48.5 mmol) in 30 mL of thionyl

chloride containing two drops of DMF was stirred at room temperature for 2 h and the excess thionyl chloride was distilled off under reduced pressure. Short-path distillation of the residue afforded 9.68 g (89%) of 3-benzyloxycyclobutanecarboxylic acid chloride: bp 110–111 °C (0.5 *mm*); IR (CCl_4) 1795 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.55 (m, 4 H), 4.02 (pent, 1 H), 4.40 (s, 2 H), 7.16 (s, 5 H).

Anal. Calcd for $C_{12}H_{13}ClO_2$: C, 64.15; H, 5.83; Cl, 15.78. Found: C, 64.47; H, 5.97; Cl, 15.59.

2,8-Bis(benzyloxy)-5,10-dioxodispiro[3.1.3.1]decane. To a stirred solution of 3-benzyloxycyclobutanecarboxylic acid chloride (9.60 g, 42.7 mmol) in 100 mL of 1:1 ether–benzene was added dry triethylamine (7.0 g, 69 mmol). The resulting suspension was refluxed under an argon atmosphere for 24 h, diluted with 60 mL of methylene chloride and poured into *aqueous 5% hydrochloric acid*. The water layer was extracted with methylene chloride (2 x 50 mL) and the organic layers were combined, washed with 1 M aqueous sodium bicarbonate, dried ($MgSO_4$) and concentrated. A mixture of 50 mL of hexanes and 10 mL of ether was added and the resulting solid triturated, and washed with hexanes to give 2.10 g of *dispirane as an off-white powder*. The filtrate was concentrated and an additional 1.80 g (48% overall yield) of product was obtained after treatment with ether–hexanes as before. An analytical sample was obtained by recrystallization from benzene: mp 139–140 °C; IR (CH_2Cl_2) 3150, 1750 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.50 (m, 8 H), 4.10 (pent, 2 H, J = 8 Hz), 4.37 (s, 4 H), 7.20 (s, 10 H).

Anal. Calcd for $C_{24}H_{24}O_4$: C, 76.57; H, 6.43. Found: C, 76.73; H, 6.32.

3-Chloro-3-nitrocyclobutanecarboxylic Acid. A solution of ethyl 3-chloro-3-nitrocyclobutanecarboxylate (1.05 g, 5.05 mmol) and sodium hydroxide (1.30 g, 7.5 mmol) in 20 mL of 4:1 ethanol-water was refluxed for 1 h, cooled and acidified with aqueous hydrochloric acid to pH 2 after addition of water (25 mL). The aqueous phase was extracted with ether (3 x 25 mL) and the combined organic layers were washed with saturated sodium chloride solution, dried ($MgSO_4$) and concentrated to give a yellow solid. Short-path distillation afforded 0.82 g (95%) of 3-chloro-3-nitrocyclobutanecarboxylic acid as a mixture of cis/trans-isomers: mp 68-70 °C; bp 122-123 °C (0.1 mm); IR (CH_2Cl_2) 3000, 1760, 1715, 1560 cm^{-1}; ^1H NMR ($CDCl_3$) 3.10 (m, 5 H, $-CH_2-$), 4.95 (m, 2 H, $C=CH_2$), 11.9 (s, 1 H, CO_2H).

Anal. Calcd for $C_5H_6ClNO_4$: C, 33.45; H, 3.37; N, 7.80; Cl; 19.74. Found: C, 33.93; H, 3.42; N, 7.66; Cl, 19.54.

3-Chloro-3-*nitrocyclobutanecarboxylic* Acid Chloride. A solution of 3-chloro-3-nitrocyclobutanecarboxylic acid (0.81 g, 4.5 mmol) in thionyl chloride (3 mL) was stirred at 25 °C for 3 h, the excess thionyl chloride was removed at reduced pressure and the product distilled to afford 0.81 g (91%) of 3-chloro-3-nitrocyclobutanecarboxylic acid chloride: bp 65 °C (0.1 mm); IR (CH_2Cl_2) 1785, 1560, 1340 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.8-3.7 (m, 5H).

Anal. Calcd. for $C_5H_5Cl_2NO_3$: C, 30.33; H, 2.54; N, 7.07; Cl, 35.81. Found: C, 30.85; H, 2.87; N, 7.23; Cl, 35.75.

3-Oxocyclobutanecarboxylic Acid Chloride. A -78 °C solution of 3-methylenecyclobutanecarboxylic acid (7.00 g, 62 mmol) in 100 mL of methanol was ozonized until the persistent blue color of dissolved ozone was noted (1 h). Dimethyl sulfide (10 mL) was added and the stirred solution allowed to warm to room temperature overnight. The solution was

concentrated by rotary evaporation, methylene chloride (50 mL) was added and the solution chilled to -10 °C. Thionyl chloride (25 mL) was introduced dropwise, and an exothermic reaction was noted during the initial stages of the addition. After the remainder of the thionyl chloride was added, the solution was refluxed for 2 h, cooled and concentrated. Short-path distillation afforded 5.40 g (65%) of 3-oxocyclobutanecarboxylic acid chloride: bp 53 °C (0.5 mm); IR (CH_2Cl_2) 1790, 1385 cm^{-1}; ^1H NMR ($CDCl_3$) 3.40 (m, 5 H).

Anal. Calcd for $C_5H_5ClO_2$: C, 45.31; H, 3.80; Cl, 26.75. Found: C, 44.88; H, 3.90; Cl, 26.86.

2,8-Dimethylene-5,10-dioxodispiro[3.1.3.1]decane. To a stirred solution of 3-methylenecyclobutanecarboxylic acid chloride[13] (21.8 g, 0.167 mmol) in 250 mL of 1:1 ether-benzene was added dry triethylamine (27.0 g, 0.267 mol) under an argon atmosphere. The resulting cream-colored suspension was stirred and refluxed for 24 h, cooled and washed with ice cold 1 M aqueous hydrochloric acid. The acidic aqueous phase was extracted with ether (2 x 25 mL) and discarded. The combined organic layers were washed with 1 M aqueous sodium bicarbonate solution, dried ($MgSO_4$) and concentrated to afford a reddish oil. This oil was triturated with hot hexanes (3 x 50 mL) and insoluble residue discarded. The hexane solution was cooled, decanted from precipitate, reheated and recooled. The product was filtered, washed with cold hexanes (50 mL) and dried in vacuo to afford 2.50 g (16%) of 2,8-dimethylene-5,10-dioxodispiro[3.1.3.1]decane. The filtrate was concentrated and the residue chromatographed on silica gel (5:1 hexane-ether eluent). The crude solid obtained was recrystallized from hexane to afford 5.4 g (34%) of additional product. Two recrystallizations from hexane gave an

analytical sample: mp 112–113 °C; IR (CH_2Cl_2) 2970, 1765, 1690 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.16 (t, 8 H, J = 3 Hz), 4.83 (t, 4 H, J = 3 Hz).

Anal. Calcd for $C_{12}H_{12}O_2$: C, 76.57; H, 6.43. Found: C, 76.51; H, 6.32.

2,5,8,10-Tetraoxodispiro[3.1.3.1]decane. A solution of 2,8-dimethylene-5,10-dioxodispiro[3.1.3.1]decane (0.48 g, 2.55 mmol) in 50 mL of methylene chloride was chilled to −78 °C and a stream of ozone in oxygen was introduced via a glass fritted bubbler using a Welsbach ozonater (T-23). The ozonolysis was continued until the persistant blue color of dissolved ozone was observed (ca. 10 min). Dimethyl sulfide (1 mL) was added and the dry-ice bath allowed to warm slowly to room temperature. The organic layer was washed with water (2 x 25 mL), dried and concentrated. The resulting solid was triturated twice with hot ether and dried in vacuo to give 0.27 g (55%) of 2,5,8,10-tetraoxodispiro[3.1.3.1]decane. Sublimation at reduced pressure *(0.10 mm) gave an analytical sample: mp* (215–220 °C, decomp); IR (KBr) 3050, 1780, 1745 cm^{-1}; ^1H NMR ($CDCl_3$–d_6DMSO) 3.53 (s).

Anal. Calcd for $C_{10}H_8O_4$: C, 62.50; H, 4.20. Found: C, 61.99; H, 4.32.

2,5,8,10-Tetraoximinodispiro[3.1.3.1]decane. A solution of 2,5,8,10-tetraoxodispiro[3.1.3.1]decane (0.476 g, 2.48 mmol), hydroxylamine hydrochloride (3.40 g, 49.2 mmol) and pyridine (4.0 g, 50 mmol) in 50 mL of absolute ethanol was refluxed for 24 h and then poured into 150 mL of water. The product was filtered and washed thoroughly with water and once with methanol and then dried to afford 0.347 g (56%) of 2,4,8,10-tetraoximinodispiro[3.1.3.1]decane. An analytical sample was recrystallized from dimethyl sulfoxide–chloroform: mp 275 °C (decomp); IR (KBr) 3170, 2930, 1400, 960, 910 cm^{-1}; ^1H NMR (d_6 DMSO/ $CDCl_3$) δ 3.10 (br s), 3.30 (br s), 10.35 (s, D_2O ex.), 10.80 (s D_2O ex.).

Anal. Calcd for $C_{10}H_{12}N_4O_4$: C, 47.62; H, 4.80; N, 22.21. Found: C, 46.43; H, 4.93; N, 20.73.

5,10-Dichloro-5,10-dinitrodispiro[3.1.3.1]decane. To a solution of 5,10-dioximinodispiro[3.1.3.1]decane (1.09 g, 5.61 mmol) in 35 mL of benzene was added 25 mL of 5.25% sodium hypochlorite (pH 5.5, adjusted with phosphoric acid). After the two-phase mixture was stirred for 1.5 h, the benzene layer was added to 50 mL of pH 10.5 commercial bleach containing tetrabutylammonium hydrogen sulfate (1.90 g, 5.60 mmol). A water bath was used for both oxidations. After for 1 h, the aqueous layer was extracted with ether (2 x 50 mL) and the combined organic layers were washed with saturated sodium chloride solution (25 mL), dried ($MgSO_4$) and concentrated to give 1.50 g of semi-solid product. Recrystallization from methylene chloride-hexanes followed by sublimation at 0.5 mm pressure gave an analytical sample of *5,10-dichloro-5,10-dinitro*dispiro[3.1.3.1]decane: mp 171-173 °C; IR (CH_2Cl_2) 1560, 1340 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.80 (m, 12 H).

Anal. Calcd for $C_{10}H_{12}Cl_2N_2O_4$: C, 40.70; H, 4.10; N, 9.49; Cl, 24.02. Found: C, 41.07; H, 4.20; N, 9.26; Cl, 24.73.

2,5,8,10-Tetrachloro-2,5,8,10-tetranitrodispiro[3.1.3.1]decane. A suspension of 2,5,8,10-tetraoximinodispiro[3.1.3.1]decane (0.220 g, 0.872 mmol) in 25 mL of methylene chloride at 0 °C was stirred while chlorine gas was introduced slowly. The resulting green solution was stirred for 30 min after the solid dissolved. The solution was concentrated and 10 mL of benzene, sodium hypochlorite (10 mL of pH 10.5, 5% NaOCl) and tetrabutylammonium hydrogen sulfate (0.50 g, 1.5 mmol) were added. The resulting two phase mixture was stirred for 1 h at 25 °C and the aqueous

layer was extracted with methylene chloride (2 x 25 mL). The combined organic layers were washed with saturated sodium chloride solution, dried ($MgSO_4$) and concentrated to afford 0.33 g of yellow solid. This solid was triturated with ether twice and recrystallized from methylene chloride to give 30 mg (8%) of 2,5,8,10-tetrachloro-2,5,8,10-tetranitrodispiro[3.1.3.1]decane: mp 218-220 °C (decomp); IR (KBr) 1570, 1550, 1350, 1145 cm^{-1}; ^1H NMR.

Anal. Calcd for $C_{10}H_8Cl_4N_4O_8$: C, 26.46; H, 1.78; N, 12.34; Cl, 31.23. Found: C, 26.32; H, 1.90; N, 12.00; Cl, 30.87.

2,5,8,10-Tetranitrodispiro[3.1.3.1]decane. Chlorine gas was introduced into a 0 °C suspension of 2,5,8,10-tetraoximinodispiro[3.1.3.1]decane (0.220 g, 0.872 mmol) and stirring was continued for 30 min after the reaction was complete. The solution was concentrated and benzene (10 mL), tetrabutylammonium hydrogen sulfate (0.50 g, 1.47 mmol) and sodium hypochlorite (10 mL of pH 10.5, 5% NaOCl) were added and the mixture was stirred for one hour. The aqueous layer was extracted with methylene chloride (2 x 20 mL) and the combined organic layers washed with 1 M sodium bicarbonate solution, dried ($MgSO_4$) and concentrated to give a solid after two ether triturations. A solution of this solid in 25 mL of tetrahydrofuran and 5 mL of water containing hydroxylamine hydrochloride (0.42 g, 6.9 mmol) was stirred while zinc powder (0.40 g, 6.0 mmol) was added slowly portionwise over a 5 min period. After a 2 h period, the solution was refluxed for one hour. The cooled solution was diluted with water and extracted with methylene chloride (2 x 25 mL). The combined organic layers were washed with saturated sodium chloride solution, dried ($MgSO_4$) and concentrated. Column chromatography of the resulting oil on silica gel using 3:1 hexane-

ethyl acetate afforded 52 mg (20%) of 2,5,8,10-tetranitrodispiro[3.1.3.1]-decane as a mixture of isomers: TLC (3:1 hexane–EtOAc) R_f = 0.10, 0.14); mp 110–112 °C; IR (KBr) 1535, 1370 cm^{-1}; ^1H NMR (CH_3CN) δ 3.0 (d, 8 H, J = 7 Hz), 5.5 (m, 4 H).

Anal. Calcd. for $C_{10}H_{12}N_4O_8$: C, 37.98; H, 3.83; N, 17.72. Found: C, 37.88; H, 3.80; N, 16.97.

1-Nitroazetidine-3-carboxylic Acid Chloride. A solution of 1-nitroazetidine-3-carboxylic acid[32] in 10 mL of thionyl chloride was stirred at room temperature for 24 h and concentrated by rotary evaporation to yield 2.30 g (96%) of 1-nitroazetidine-3-carboxylic acid chloride. An analytical sample was obtained by molecular distillation of a small sample: bp 105 °C (0.5 mm); IR (CH_2Cl_2) 1800, 1540, 1340, 1260 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.90 (pent, 1 H, J = 6 Hz), 4.50 (d, 4 H, J = 6 Hz).

Anal. *Calcd for* $C_4H_5N_2ClO_3$: C, 29.20; H, 3.06; N, 17.02; Cl, 21.54. Found: C, 28.85; H, 3.09; N, 17.01; Cl, 20.92.

3,3-Dinitrocyclobutanecarboxylic Acid Chloride. A solution of 3,3-dinitrocyclobutane-1-carboxylic acid (0.88 g, 4.63 mmol) in 5 mL of thionyl chloride was stirred at room temperature for 2 h and the excess thionyl chloride was removed at reduced pressure. Short-path distillation of the residue gave 0.72 g (75%) of 3,3-dinitrocyclobutanecarboxylic acid chloride: bp 85–87 °C (0.2 mm); IR (CH_2Cl_2) 1790, 1560, 1330 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.50 (m, 1 H), 3.60 (br s, 4 H).

Anal. Calcd for $C_5H_5ClN_2O_5$: C, 28.79; H, 2.42; N, 13.43; Cl, 17.00. Found: C, 28.83; H, 2.47; N, 12.64; Cl, 17.38.

III. 1,3,3-TRINITROAZETIDINE

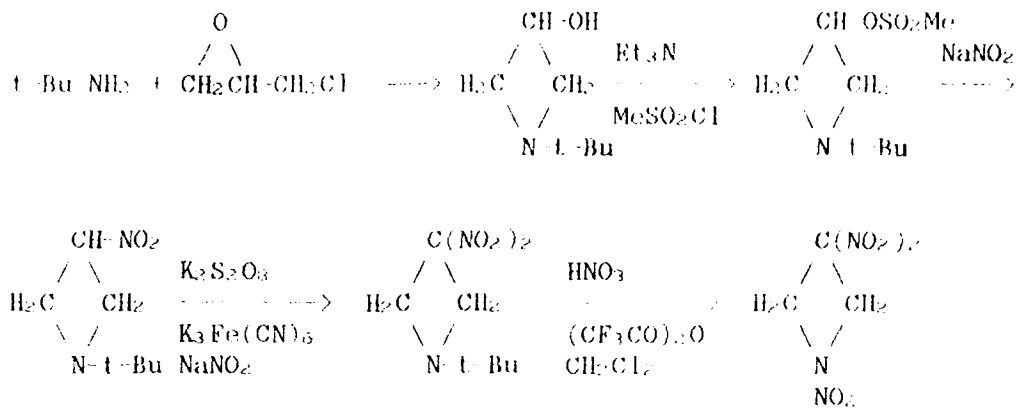
A. Discussion

The first synthesis of 1,3,3-trinitroazetidine (TNAZ) was carried out at Fluorochem, Inc., under support from ONR.[37] Subsequently, a preliminary process improvement program was carried out under sponsorship of ARDEC.[38] The present work, with ARDEC funding and ONR administration, had as objectives the preparation of sufficient TNAZ To complete additional stability and performance tests, and the development of new synthetic techniques to provide significant yield improvements.

TNAZ is a unique compound containing both *gem*-dinitro and nitramino groups in a four-membered-ring. The small ring gives the molecule approximately 25 Kcal/mol of ring strain energy which adds significantly to TNAZ's performance. Based on combustion studies, the heat of formation of TNAZ is calculated to be 8.7 Kcal/mol, with a monopropellant I_{sp} (1000-14.7 psi) of 273.5 sec[39] (HMX is 267.4 sec).

TNAZ melts at 101 °C and is thermally stable above 240 °C. From the x-ray structure,[40] the estimated the density of TNAZ is 1.84 g/cm^3 at 20°C. (The observed density of TNAZ by silver nitrate flotation is 1.83 g/cm^3). The structure of TNAZ has two very interesting features. The azetidine ring is puckered by 13.6° which results in the nitramino nitrogen having essentially pure sp^3 hybridization. The nitro group on the azetidine nitrogen has a very high out of plane deformation of 39.4° yet a short N-N bond distance of 1.351 A. This short distance compares favorably with the shortest N-N bond distances in RDX or HMX and may help explain the stability of TNAZ.

The synthesis of TNAZ is outlined in the following equation starting with inexpensive and readily available starting materials:



During this program, several of these steps were reinvestigated in an effort to improve yields, facilitate material handling, minimize waste disposal problems, and increase safety. Other routes to TNAZ were also investigated briefly.

Step 1. 1-*t*-Butyl-3-hydroxyazetidinium Hydrochloride. The reaction of t-butylamine with epichlorohydrin to give the 3-hydroxyazetidine involves two distinct steps. First, the amine and epoxide condense to form a 1-amino-3-chloropropanol which then cyclizes to give the desired product. Different solvents appear to be required for each step. The condensation reaction was studied in methylene chloride, hexane, acetonitrile and Freon 113. The reactions were monitored by following the disappearance of epichlorohydrin by glc. The yields in these reactions varied from 20 to 69% and are summarized in Table 1. The best yields were obtained in hexane or without solvents. On a small scale, this condensation could be run neat, but on a kilogram scale, uncontrollable exotherms were observed.

The use of acid or base catalysts was investigated. The presence of *p*-toluenesulfonic acid did not effect the condensation reaction and caused

the cyclization reaction to fail. The presence of potassium *t*-butoxide in one attempt gave no improvements in yield. The use of excess t-butylamine was also found to be ineffective in improving the yield.

Table 1. Synthesis of 1-t-Butyl-3-hydroxyazetidine - Solvent Effects

Run #	Solvent	Condensation %	Product yield %	Notes
1	hexane	50	60	
2	hexane	50	0	a
3	acetonitrile	60	39	
4	CH_2Cl_2	50	22	
5	CH_2Cl_2	50	0	a
6	CH_2Cl_2	80	57	b
7	- (neat)	80	53	

Reactions run with 0.1 mol t-butylamine and 0.1 epichlorohydrin
a p-Toluenesulfonic acid
b 0.2 mol t-butylamine

The cyclization reaction requires the use of a mildly basic solvent such as acetonitrile. Methylene chloride or methanol was not effective. The use of acetonitrile in the condensation step led to lower yields. Thus, the best results were obtained from reactions conducted first in concentrated hexane solutions for 3 days at room temperature, and after removal of the hexane, in refluxing acetonitrile for 3-6 hours. Yields of 69% at the 1 kg scale were obtained by this method (Table 2).

Table 2. Synthesis of 1-t-Butyl-3-hydroxyazetidine

RUN	solvent	t-Butylamine g (mole)	Epichlorohydrin g (mole)	Yield I g (%)
1.	hexane	980 (13.4)	1300 (13.4)	1365 (61.7)
2.	hexane	980 (13.4)	1300 (13.4)	1250 (56.5)
3.	hexane	980 (13.4)	1300 (13.4)	1400 (65)
4.	hexane	974 (13.3)	1235 (13.3)	900 (41)
5.	neat	115 (1.5)	140 (1.5)	175 (68)
6.	neat	570 (7.8)	720 (7.8)	892 (68)

All runs included post-treatment with refluxing acetonitrile.

Step 2. 1-t-Butyl-3-methanesufonylazetidine. The mesylate is prepared from the 3-hydroxyazetidine hydrochloride and *methanesulfonyl* chloride in methylene chloride with 2 moles of triethylamine. The mesylates prepared in this manner contained uncharacterized impurities which were removed after later steps. The crude mesylate is easily purified by trituration with ether; the impurities are insoluble. The purified mesylate is suitable for direct reaction in the next step without further treatment.

Table 3. Synthesis of 1-t-Butyl-3-methanesulfonylazetidine.

RUN	1 g (mole)	Triethylamine g (mole)	CH_3SO_2Cl g (mole)	Yield[a] g (%)	Note
1.	574 (3.5)	723 (7.1)	439.5 (3.84)	637 (88)	
2.	574 (3.5)	723 (7.1)	439.5 (3.84)	650 (90)	
3.	574 (3.5)	723 (7.1)	439.5 (3.84)	588 (81)	
4.	574 (3.5)	723 (7.1)	439.5 (3.84)	703 (95)	
5.	100 (0.60)	126 (1.2)	76.0 (0.67)	80 (64)	b
6.	115 (0.693)	144 (1.4)	87.0 (0.764)	118 (84)	
7.	250 (1.5)	315 (3.1)	190.9 (1.674)	220 (71)	
8	250 (1.5)	315 (3.1)	190.9 (1.674)	220 (71)	
9.	100 (0.60)	62 (0.6)	76.0 (0.67)	120 (95)	c
10.	574 (3.5)	723 (7.1)	439.5 (3.84)	400 (55)	b
11.	60 (0.364)	75 (0.77)	45.8 (0.4)	445 (60%)	b,d

a. Crude yields
b. Product purified by Ether treatment
c. Freon as solvent
d. DMAP (dimethyaminopyridine) in place of triethylamine

The use of dimethylaminopyridine as a replacement base for triethylamine in the mesylate formation reaction was investigated. No significant difference in yield or reaction time was noted which would justify the use of this more expensive base. In one run, the use of Freon 113 as the reaction solvent in place of methylene chloride gave no difference in product yield or purity. As previously noted, the mesylate solutions are

unstable and were used immediately after preparation. Table 3 summarizes results obtained for the mesylation reaction during this program.

Step 3. 1-t-Butyl-3-nitroazetidine. The critical step for the scale-up of TNAZ has been the nitrite displacement of the mesylate to give the mononitro derivative. We now find that using a two-phase medium, water and Freon 113, results in a controlled, large-scale reaction, without the need for the nitrite scavenger, phloroglucinol. Although reaction times are somewhat longer (1-3 days) than previously observed for water-methanol solutions (16-24 hours), the isolated yield of mononitroazetidine from the Freon solution is 55-65% (compared to 30-35% in methanol-water). In addition, the mononitro derivative can be reacted further, without isolation from the Freon 113 solution, to give the dinitro intermediate. The overall yield of the dinitroazetidine starting from the mesylate has been improved by these changes from 18% to 35% (Table 4).

Table 4. Synthesis of 1-t-Butyl-3-nitroazetidine.

RUN	mesylate g (mol)	Phloroglucinol g (mol)	Solvent	Yield g (%)	crude
1.	600 (2.9)	335 (2.067)	CH_3OH	130	(38)
2.	600 (2.9)	335 (2.067)	CH_3OH	130	(38)
3.	580 (2.8)	257 (1.586)	CH_3OH	125	(38)
4.	80 (0.386)	35 (0.216)	CH_3OH	38	(63)
5.	80 (0.386)	35 (0.216)	CH_3OH	15	(25)
6.	15 (0.072)	0	Freon 113	6	(50)
7.	6 (0.029)	0	Freon 113	2	(50)
8.	20 (0.097)	0	Freon 113	7	(50)
9.	230 (1.116)	0	Freon 113	92	(52)
10.	100 (0.483)	0	Freon 113	39	(50)
11.	800 (3.866)	0	Freon 113	450	(65)

The effect of halide ion on the displacement reaction was investigated. Parallel reactions of crude mesylate with 2 equivalents of nitrite were studied in methanol-water solvents. In the absence of other counter ions,

these materials gave 35-38% yields of mononitro product. The addition of 1 equivalent of potassium iodide gave a 29% yield, whereas 0.25 equivalents of sodium bromide gave 35% of the mononitro compound. These deviations may have resulted from work-up variations rather than any counter-ion effect. Increasing the nitrite concentration to 12 equivalents similarly failed to improve the yield.

Mononitroazetidine has both secondary nitro and tertiary amine functionality and can be dissolved either in acid, by forming an ammonium salt, or in base, by forming an nitronate salt. It is likely that some of the product is lost in the water layer because of incomplete extraction due to one or both of these salt formation reaction. In a brief pH study, solutions carefully adjusted to pH 7.5-8.5 were found to give about 10% additional product upon exhaustive extraction.

Table 5. Synthesis of 1-t-Butyl-3,3-dinitroazetidine.

RUN	mononitro g (mol)	Dinitro g (crude)	Dinitro salt g	Yield of Dinitro[a] g (%)
1.	50 (0.31)	30	38.0	22.6 (36)
2.	110 (0.69)	70	60.0	35.6 (25)
3.	115 (0.723)	73.5	56	33.3 (24)
4.	80 (0.503)	65	50	30 (33)
5.	40 (0.25)	32	24	14.3 (28)
6.	240 (1.509)	180	130	77.3 (26)
7.	25 (0.157)	34	36	21.4 (67)[b]

a. based on mesylate
b. Distilled mononitro, yield this step only.

Step 4. Synthesis of 1-t-Butyl-3,3-dinitroazetidine. Procedures for persulfate catalyzed oxidative nitration of 3-nitroazetidine to 3,3-dinitroazetine were not changed during this program, and the results of seven

runs are found in Table 5. The yields based on mesylate were between 24% and 36%. In one case, the mononitro compound was purified by distillation under high vacuum prior to reaction, and the yield of 67% was consistant with that previously observed.

Step 5. Nitrolysis to TNAZ. The trifluoroacetate salt of dinitroazetidine was nitrolyzed in methylene chloride with trifluoroacetic anhydride and 100% nitric acid. No changes were made in this reaction procedure. During prior programs only milligram quantities of TNAZ had been isolated and the work involved the use of methylene chloride solutions only. However, during this program procedures were developed for isolating and purifying TNAZ. In general, the nitrolysis mixture was washed with water and 5% sodium bicarbonate solution and dried over magnesium sulfate, and then evaporated to give crude TNAZ in 95-98% yield. This material, which was slightly yellow in color and had less than 1% impurities by nmr, was recrystallized twice from methylene chloride and the purified TNAZ was isolated in 82-87% yield (Table 6). TNAZ obtained in this way was almost colorless and was further dried under high vacuum for 12 hours to remove any residual solvents. During this program 144 g of TNAZ was prepared and shipped to ARDEC.

Table 6. Nitrolysis to TNAZ

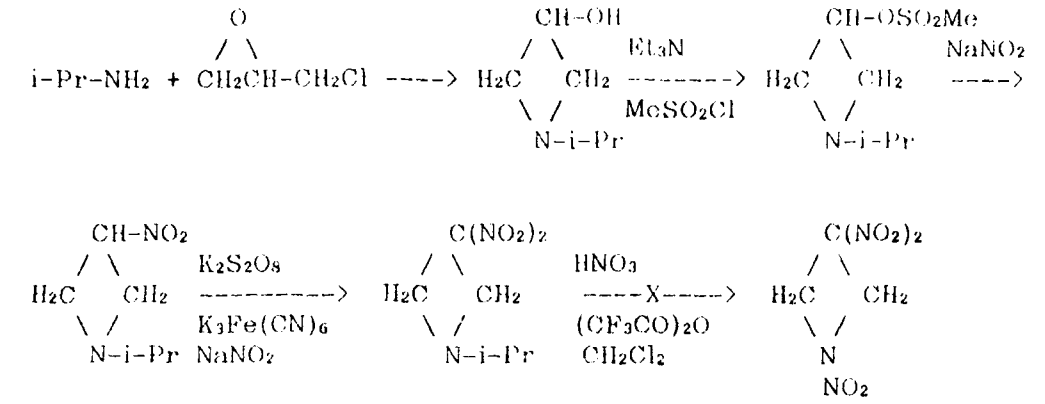
RUN	Dinitro Salt g (mol)	Yield TNAZ g (%)
1.	38.0 (0.135)	22.4 (99)
2.	63.4 (0.224)	36 (84)
3.	101 (0.359)	60 (87)
4.	50 (0.178)	26 (82)

Analysis of TNAZ and Its Intermediates. New analytical methods for following these reactions have been developed using gas chromatography on an OV-17 column with Helium carrier gas, thermal conductivity detector, and 250 °C injector and detector temperatures. For analysis of the mono and dinitroazetidine intermediates the column temperature was programmed from 100 to 240 °C at 8 °C/min.

TNAZ is not very soluble in deuterochloroform so the ^1H NMR spectra were recorded in acetone-d6 in which it shows a singlet at δ 5.2. The ^{13}C NMR of TNAZ shows two absorbance at δ 103.4 and 63.4. The IR spectrum in methylene chloride shows nitro group absorbance at 1580 and 1420 cm^{-1}.

Alternative Routes to TNAZ. The existing route to TNAZ uses the bulky t-butyl group as a blocking group until the final nitrolysis. Although this steric bulk helps stabilize the azetidine ring, it may also hinder other reaction such as the nitrite displacement. During this program, we investigated the possibility that the less sterically demanding isopropyl group might be substituted.

The reaction of isopropylamine with epichlorohydrin gave 1-i-propyl-3-hydroxyazetidium hydrochloride in 25-30% yield.[41] This alcohol was converted to the mesylate[42] in 83% yield and reacted with nitrite to give the mononitro compound in 26% yield. Oxidative nitration of the mononitro compound gave 3,3-dinitro-1-i-propylazetidine in 17% yield. In each case the yield was found to be less than that for the corresponding t-butyl derivative. Nitrolysis of the 3,3-dinitro compound failed to give TNAZ under conditions used for t-butyl nitrolysis. This route was not investigated further.



B. Experimental

WARNING: All nitro compounds are potentially thermally unstable. TNAZ is shock sensitive. Use appropriate shielding on reactions described below.

Reaction mixtures were analyzed by glc: Column 3% OV-17 on G.C.Q. 80/100; helium carrier gas; injector 250 °C Detector (hot wire) 300 °C; temperature program 120 °C (2 min) then increased at 8 °C/min to 240 °C. Relative times: 1-*t*-butyl-3-nitroazetidine, 2 min; 1-*t*-butyl-3,3-dinitroazetidine, 3.5 min; TNAZ, 5.5 min.

1-*t*-Butyl-3-hydroxyazetidinium Hydrochloride. To a mechanically stirred solution of epichlorohydrin (756 g, 8.18 mol) in hexanes (bp 70-85 °C, 4 L) in a 12 liter flask, was added t-butylamine (572 g, 824 mL, 7.84 mol), portionwise, over 2 h. The solution was stirred for 3 days at 20-25 °C. The hexanes were removed by distillation at 50-60 °C (30 mm), and the residual materials redissolved in acetonitrile (2 L) and refluxed for 16 h. The solution was cooled and filtered to give 550-650 g of solid. The filtrate was diluted with 300 mL of ether, cooled and filtered to give another 50-100 g of solid. The combined solids were washed with 2 x 150

mL of ether and dried *in vacuo* to give 730 g (55%) of 1-*t*-butyl-3-hydroxyazetidinium hydrochloride.

1-*t*-Butyl-3-methanesulfonylazetidine. Methanesulfonyl chloride (439 g, 3.8 mol) was added, dropwise, to a stirred mixture of triethylamine (723 g, 7.1 mol) and 1-*t*-butyl-3-hydroxyazetidinium hydrochloride (574 g, 3.5 mol) in CH_2Cl_2 (2 L) at -20 °C. After the addition was completed, the stirring was continued and the temperature allowed to rise to 25 °C over 3 h. Then, water (500 mL) was added and the organic layer was separated, washed with water (2 x 150 mL), dried ($MgSO_4$) and evaporated at 30 °C (30mm) to give 600 g (83%) of 1-*t*-butyl-3-methanesulfonylazetidine, as a crude oil: ^1H NMR δ 1.2 (s, 9 H, CH_3); 3.5 (4 H, CH_2); 3.1 (3 H, OSO_2CH_3); 5.0 (1H). The crude oil was triturated with 350 mL of ether, filtered and evaporated at 35 °C (20 mm) to give 400 g (55%) of pure mesylate suitable for use in the next step.

1-*t*-Butyl-3-nitroazetidine. A solution of sodium nitrite (1.3 kg, 17.4 mol) in water (2.1 L) was stirred with a solution of 1-*t*-butyl-3-methanesulfonylazetidine (800 g, 3.8 mol) in Freon 113 (2 L) at 25 °C for 64 h. The course of the reaction was monitored by ^1H NMR. The layers were separated, and the water layer was extracted with CH_2Cl_2 (2 x 100 mL). The combined extracts were dried ($MgSO_4$) and evaporated at 30 °C (30 mm) to give 400 g (65%) of essentially pure 1-*t*-butyl-3-nitroazetidine. An analytical sample was obtained by distillation, bp 50-52 °C (0.1 mm): IR (CH_2Cl_2) 3000 (C-H), 1550, 1430 cm^{-1} (NO_2); ^1H NMR ($CDCl_3$) δ 0.95 (s, 9 H, CH_3), 3.55 (asym d, J=3 Hz, 4 H, CH_2), 4.90 (quint, J=3 Hz, 1 H).

1-*t*-Butyl-3,3-dinitroazetidine. A mixture of 1-*t*-butyl-3-nitroazetidine (43 g, 0.259 mol) and sodium hydroxide (11.3 g, 0.275 mol) in water (66 mL)

was stirred at 25 °C until a homogeneous solution formed. This solution was cooled to 5 °C and a chilled solution of sodium nitrite (90 g, 1.3 mol) and potassium ferricyanide (17 g, 0.051 mol) in water (600 mL), followed by solid sodium persulfate (87.0 g, 0.369 mol), was added. The temperature rose to 25 °C after 15 min and the mixture was stirred for 1 h, and then was extracted with CH_2Cl_2 (3 x 150 mL). The combined extracts were dried ($MgSO_4$) and the solvent evaporated to give 39.1 g (70 %) of 1-*t*-butyl-3,3-dinitroazetidine. This material was dissolved CH_2Cl_2 (60 mL) and trifluoroacetic acid (24 mL) added, and the precipitate was filtered and dried *in vacuo* to give 50 g of 1-*t*-butyl-3,3-dinitroazetidinium trifluoroacetate, mp 150 °C dec. NMR of free amine: δ 1.0 (s, 9 H) and 4.2 (s, 4 H); salt: δ 1.5 (s, 9 H) and 4.2 (s, 4 H).

1,3,3-Trinitroazetidine (TNAZ). A solution of trifluoroacetic anhydride (150 g, 100 mL, 0.71 mol) in CH_2Cl_2 (150 mL) was cooled to -10 °C, and 100% nitric acid (45 g, 30 mL, 0.71 mol) was added, dropwise, over 10 min at a rate such that reaction temperature did not exceed -5 °C. This solution was stirred for 10 min and solid 1-*t*-butyl-3,3-dinitroazetidinium trifluoroacetate (31.7 g, 0.1 mol) was added, portionwise, over 20 min. The mixture was stirred for 2 h at -5 °C, and then filtered to remove approximately 6 g of pure TNAZ. The reaction mixture then was diluted cautiously with water (300 mL). The organic layer was washed with water (2 x 100 mL) and 5% aqueous sodium carbonate (50 mL), dried ($mgSO_4$), and evaporated to give 11.6 g (for total of 17.6 g, 98%) of essentially pure 1,3,3-trinitroazetidine, mp 95-97 °C. An analytical sample was prepared by recrystallization from CH_2Cl_2, mp 101 °C: IR (CH_2Cl_2): 3050 (C-H), 1580, 1420 (NO_2) cm^{-1}; NMR ($CDCl_3$): δ 5.2 (s) ppm.

1-Isopropyl-3-nitroazetidine. A solution of sodium nitrite (119 g, 1.6 mol) in water (180 mL) was added to a solution of 1-isopropyl-3-methanesulfonylazetidine (128 g, 0.72 mol)[42] in methanol (320 mL), and then phloroglucinol dihydrate (55 g) was added. The mixture was stirred at 25 °C for 25 h and then was extracted with ether. The organic layer was dried ($MgSO_4$), and evaporated to give 25 g (26%) of 1-isopropyl-3-nitroazetidine as dark brown crude oil. ^1H NMR δ ($CDCl_3$) 0.9-1.0 (d, J = 7 Hz, 6 H), 2.2-2.9 (m, 1 H), 3.5-3.8 (d, 4 H), 4.9-5.0 (t, 1 H).

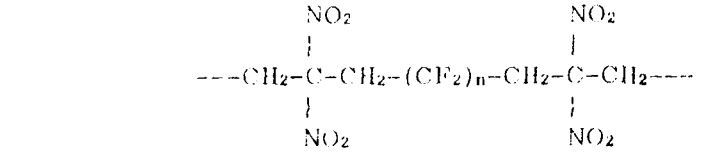
1-Isopropyl-3,3-dinitroazetidine. A mixture of 1-isopropyl-3-nitroazetidine (22 g, 0.14 mol) and sodium hydroxide (6.4 g, 0.16 mol) in water (70 mL) was stirred at 25 °C until a clear solution formed. This solution was cooled to 5 °C and a chilled solution of sodium nitrite (47 g, 0.6 mol) and potassium ferricyanide (8.8 g, 0.03 mol) in water (340 mL) was added followed by solid sodium persulfate. The temperature rose to 35 °C after 15 min and the mixture was stirred for 1 h. The reaction mixture was extracted with methylene chloride (3 x 150 ml), dried ($MgSO_4$) and concentrated to give 5 g (17%) of 1-isopropyl-3,3-dinitroazetidine as a light brown oil: ^1H NMR δ ($CDCl_3$) 0.9-1.0 (d, 6 H), 2.2-2.8 (m, 1H), 3.9 (s, 4 H). This material was dissolved in ether (100 mL) and trifluoroacetic acid (14 mL) was added. The precipitate was filtered and dried *in vacuo* to give 1-isopropyl-3,3-dinitroazetidinium trifluoroacetate as yellow solid.

IV. FLUORONITRO POLYMERS

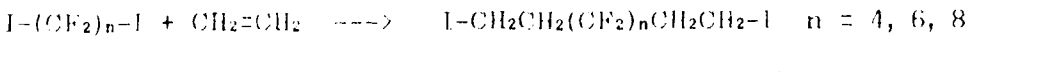
A. Discussion

Fluorinated polymers with nitro substituents are needed for use as binders for pyrotechnic applications. Ideally, such a binder would contain a high percent of fluorine, and no hydrogen since hydrogen degrades the performance of flares. The binder should be stable thermally and must be chemically compatible with reactive metals.

The ideal monomer system would contain *gem*-dinitro functionality next to difluoromethylene groups and these groupings would be separated by a single methylene group from the functionality used to link the monomeric sections (e.g. isocyanate or hydroxyl). Thus, chemically stable systems with minimum hydrogen content could be obtained. Unfortunately, no practical routes have been reported to compounds containing the adjacent *gem*-dinitro-*gem*-difluoro structure.[1] As a result, we have investigated the synthesis of more accessible monomers containing *gem*-dinitro groups and *gem*-difluoro groups with one intervening methylene group.



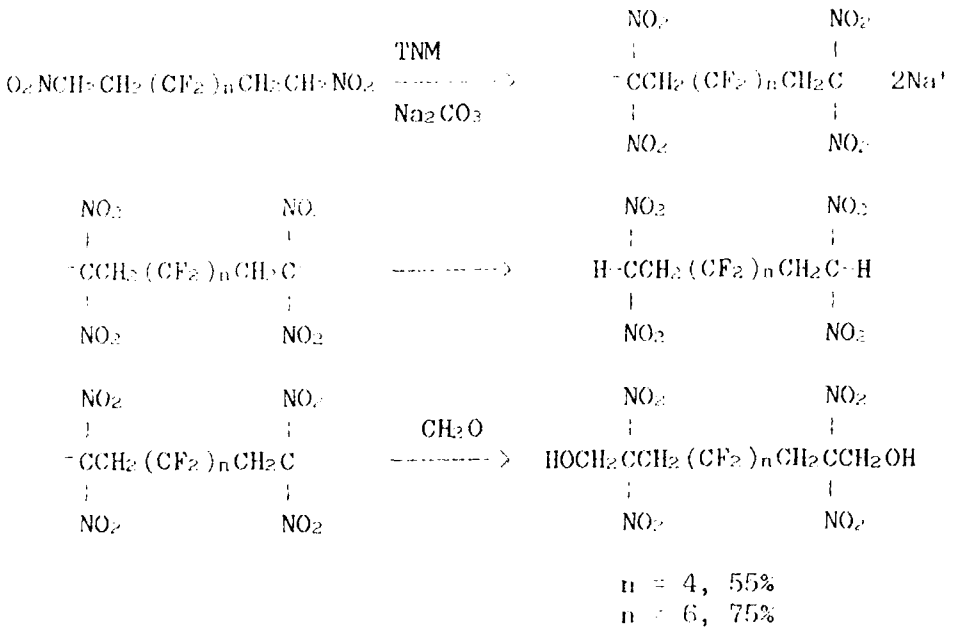
A synthetic entry to this system was described in a previous interim report.[1] The reaction of α,ω-diiodoperfluoroalkanes with ethylene gives the corresponding ethylene insertion products which are reacted further with nitrite ion to afford the α,ω-bis(nitroethyl)perfluoroalkanes.



The ethylene insertion reaction is essentially quantitative. Previously, the nitrite displacement reaction was conducted in DMF and yields of 20-40% were obtained. Yields of the dinitro compounds were improved to 40-60% by using DMSO as the solvent. The remainder of the starting diiodides were converted through intermediate nitrite esters to alcohols. Attempts to improve the nitro-nitrite ratio by the use of nitrite-saturated Amberlite IRA-900 resin were unsuccessful. Attempts to improve yields by converting the alcohols to the corresponding mono and ditosylates and reacting them with sodium nitrite, were also unsuccessful.

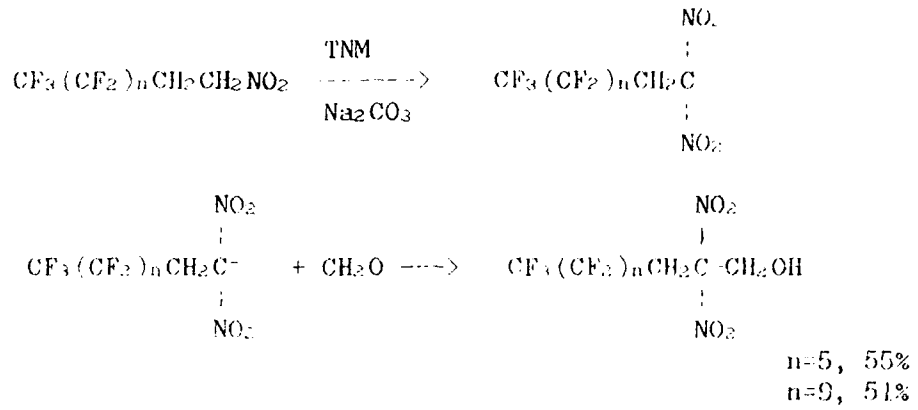
The intervening methylene group of this series allowed oxidative nitration to proceed, although under very limited conditions. Standard ferricyanide-persulfate procedures which we had found satisfactory with the mononitro model systems, failed for the α,ω-dinitro compounds. Kaplan-Shechter silver nitrate-sodium nitrite procedures failed in all cases. Reaction of the α,ω-dinitro compounds with sodium carbonate and tetranitromethane over 18-30 hours gave good yields of the $\alpha,\alpha,\omega,\omega$-tetranitro disodium salts. The intermediate salts were isolated by filtration, and careful acidification with hydrochloric acid gave the corresponding tetranitro compounds, 1,1,8,8-tetranitro-1H,2H,2H,7H,7H,8H-perfluorooctane and 1,1,10,10-tetranitro-1H,2H,2H,9H,9H,10H-perfluorodecane. These terminal *gem*-dinitro compounds were difficult to purify. The proton NMR of these tetranitro compounds showed protons on carbon bearing two nitro groups near δ 7.0. In acetone-d6, the tetranitro octane (n = 4) consistently showed about half the expect proton absorbency, perhaps indicating nitronic acid formation. In acetonitrile-d3 the spectrum was normal.

The tetranitro disodium salts were reacted with aqueous formaldehyde to give the corresponding diols, 2,2,9,9-tetranitro-1H,1H,3H,3H,8H,8H,10H,-10H-perfluorodecane-1,10-diol and 2,2,11,11-tetranitro-1H,1H,3H,3H,10H,10H,-12H,12H-perfluorododecane-1,12-diol, in yields of 75 and 55%, respectively, based on the starting α,ω-dinitro compounds. These tetranitro diols are highly crystalline and stable.

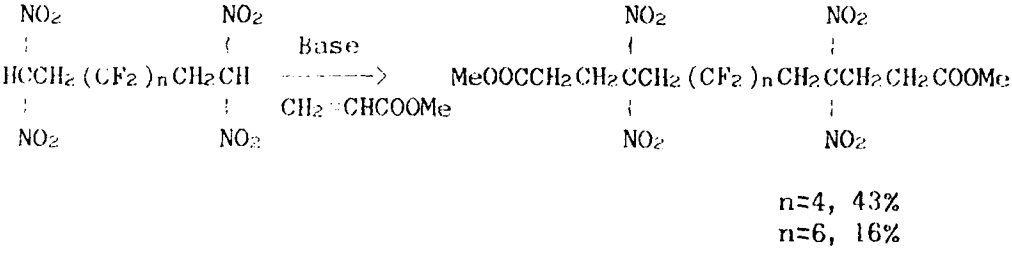


n = 4, 55%
n = 6, 75%

Similar *gem*-dinitro compounds were also prepared from 1-nitro-1H,1H,2H,2H-perfluorooctane and dodecane in 68% and 50% yields, respectively. Formylation of these dinitro compounds gave the corresponding alcohols in 55% and 51%.



The reaction of 1,1,4,4-tetranitrobutane,[43] or its formaldehyde adduct, with two moles of methyl acrylate is the synthetic route to the polynitro diacid, diamine and diisocyanate. The fluorine-containing tetranitro disodium salts prepared here, are a potential source of similar compounds containing a central polyfluoromethylene block. Therefore, we investigated the Michael reactions of these salts with methyl acrylate.



The presence of fluorine appears to deactivate the tetranitro salts toward additions. Methyl acrylate reacted with 1,1,8,8-tetranitro-1H,2H,-2H,7H,7H,8H-perfluorooctane to give the bis-acrylate addition product, dimethyl 6,6,7,7,8,8,9,9-octafluoro-4,4,11,11-tetranitrotetradecanedioate, in low yield under most conditions. The best results were obtained by reacting the dinitro compounds with excess methyl acrylate using 1

Table 7. Conversion of Tetranitro Compound (n = 4) to Diester

RUN	MOLE RATIO[a]	SOLVENT	BASE[b]	TIME	TEMP °C	YIELD %
1	1:5	90% MeOH 10% H_2O	NaOH (0.5)	12 h	50-55	0
2	1:3.3	90% MeOH 10% H_2O	NaOH (4.3)	20 h	50	13
3	1:5	90% MeOH 10% H_2O	NaOH (1.9)	6 h	50	17
4	1:5	90% MeOH 10% H_2O	NaOH (0.5)	66 h	70	5
5	1:2	THF	BuLi (2.0)	2 h	-70	0
6	1:10	CH_3CN	KF[c] (.3)	22 h	25	0
7	1:5	CH_3CN	DBU (1.0)	18 h	50	0
8	1:5	85% THF 15% H_2O	TRITON B (5.0)	16 h	70	9
9	1:5	DMF	KF (0.5)	66 h	70	8
10	1:10	80% Dioxane 20% H_2O	Triton B (1.0)	20 h	60	54

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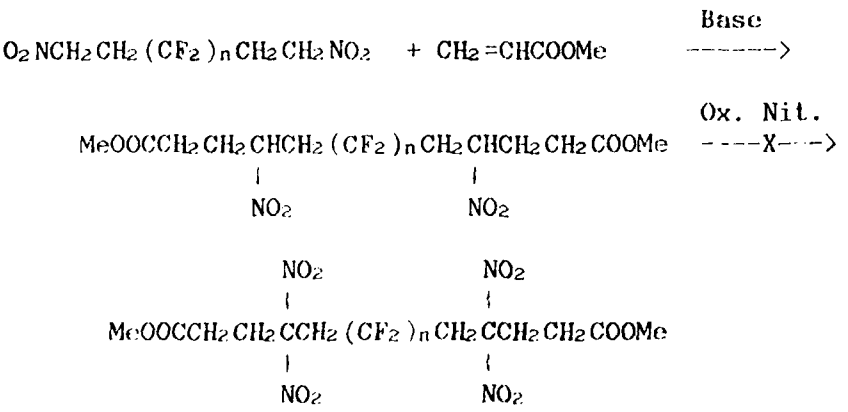
a. Mole ratio tetranitro compound:methyl acrylate
b. equivlents of base per equivalent of tetranitro compound.
c. Bu_4NCl used as phase transfer catalyst

equivalent of Triton B[44] in 80% aqueous dioxane at 60 °C for 20 hours; under these conditions, the isolated yield of the diadduct was 45%. In 85% aqueous THF, the yield dropped to 9% using the same catalyst. Other bases were examined. The reagent used for the tetranitrobutane ester preparation, sodium hydroxide in aqueous methanol, gave a 17% yield in this system. Attempted low temperature reactions involving deprotonation with

butyl lithium failed to give adducts. The use of anhydrous potassium fluoride in DMF, or the hydrate in acetonitrile[45] gave low yields. Similarly, DBU was ineffective in catalyzing this reaction. The effect of reaction conditions is summarized in Table 7.

Similar difficulties were encountered in the conversion of 1,1,10,10-tetranitro-1H,2H,2H,9H,9H,10H-perfluorodecane to the corresponding bis-Michael adduct, dimethyl 6,6,7,7,8,8,9,9,10,10,11,11-dodecafluoro-4,4,13,13-tetranitrohexadecanedioate, where the best yield obtained was 17%.

An alternative approach to the synthesis of these adducts was investigated in which the Michael reaction of methyl acrylate with the α,ω-dinitro compounds is followed by oxidative nitration. As expected, 1,8-dinitro-1H,1H,2H,2H,7H,7H,8H,8H-perfluorooctane reacted with two equivalents of methyl acrylate in the presence of DBU to give the symmetric diadduct, dimethyl 4,11-dinitro-6,6,7,7,8,8,9,9-octafluorotetradecanedioate, in 37% yield. A similar reaction in the presence of excess methyl acrylate gave the tetra-adduct, dimethyl 4,11-bis(2-methoxycarboxyethyl)-4,11-dinitro-6,6,7,7,8,8,9,9-octafluorotetradecanedioate. Attempted oxidative nitrations of the symmetric diadduct were unsuccessful under a variety of standard conditions.



B. Experimental

1-Nitro-1H,1H,2H,2H-perfluorooctane. A solution of 1-iodo-1H,1H,2H,2H-perfluorooctane (16.5 g, 34.8 mmol), sodium nitrite (6.0 g, 87 mmol) and urea (5.5 g, 92 mmol) in DMF (350 mL) was stirred at ca. 0 °C for 4 h. Phloroglucinol monohydrate (7.0 g, 43 mmol) was added and the mixture was stirred at room temperature for an additional 16 h. The reaction mixture was diluted with diethyl ether and poured over crushed ice and water. The organic layer was separated and the aqueous layer was extracted with diethyl ether (3x). The combined ethereal layers were washed with water, sodium sulfite, water (2x), and brine (2x), dried, filtered and evaporated under reduced pressure to give 10.7 g of a brown oil. The oil was impregnated on silica gel and chromatographed over silica gel (90% dichloromethane/hexane) to give 3.7 g (27%) of 1-nitro-1H,1H,2H,2H-perfluorooctane as a white solid: mp 27-29 °C; IR (CH_2Cl_2) 2970, 1550 and 1100-1300 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.6-3.4 (m, 2 H), 4.90 (t, J = 7 Hz, 2 H); ^{19}F NMR (Freon 113) ø 80.4 (3 F), 111.6 (2 F), 120.0 (6 F), and 123.6 (2 F).

Anal. Calcd for $C_8H_4F_{13}NO_2$: C, 24.44; H, 1.02; N, 3.56; F, 62.83.

Found: C, 24.70; H, 1.07; N, 4.01; F, 62.86.

1,1,8,8-Tetranitro-1H,2H,2H,7H,7H,8H-perfluorooctane. A mixture of 1,8-dinitro-1H,1H,2H,2H,7H,7H,8H,8H-perfluorooctane (0.73 g, 2.1 mmol) and potassium carbonate (1.3 g, 9.6 mmol) in methanol was stirred at room temperature for 30 min. Tetranitromethane (3.2 g, 16.3 mmol) was added over 30 min and the mixture was stirred at room temperature for 36 h. The reaction mixture was diluted with dichloromethane (400 mL), filtered,

and the solid washed with dichloromethane. The yellow solid was dissolved in water (ca. 200 mL), cooled (ca. 5 °C), and acidified with cold 10% HCl. The aqueous layer was extracted with diethyl ether (3 x 100 mL) and the combined ethereal layers were washed with water (3 x 200 mL), dried ($MgSO_4$), filtered and evaporated under reduced pressure to give a light brown solid (0.77 g). Recrystallization of the crude product from diethyl ether/hexane gave 0.63 g (68%) of 1,1,8,8-tetranitro-1H,2H,2H,7H,7H,8H-perfluorooctane as a beige solid: mp 104-105 °C (from dichloromethane/hexane); IR (CH_2Cl_2) 1595 cm^{-1}; ^1H NMR (acetone-d_6) δ 7.48 (t, J = 8 Hz, 1.0-1.7 H), 3.88 (m, 4 H); ^1H NMR (acetonitrile-DCCl$_3$) δ 7.5 (t, J = 8 Hz, 2 H), 5.9 (m, 4 H) ^{19}F NMR (acetone-d_6) ø 107.7 (m, 2 F), 118.1 (m, 2 F).

Anal. Calcd for $C_8H_6F_8N_4O_8$: C, 21.93; H, 1.38; N, 12.79; F, 34.69. Found: C, 22.08; H, 1.38; N, 12.49; F, 33.21, 35.55.

1,1,10,10-Tetranitro-1H,2H,2H,9H,9H,10H-perfluorodecane. *In a manner* similar to that described above, reaction of 1,10-dinitro-1H,1H,2H,2H,9H,9-H,10H,10H-perfluorodecane (1.0 g, 2.2 mmol) with tetranitromethane (3.5 g, 17.8 mmol) in methanol (80 mL) in the presence of potassium carbonate (1.42 g, 10.3 mmol) gave, after recrystallization from hexane/ether, 0.60 g (50%) of 1,1,10,10-tetranitro-1H,2H,2H,9H,9H,10H-perfluorodecane: mp 131-133 °C; ^1H NMR (acetone-d_6) δ 6.95 (t, 2 H, J = 7 Hz), 3.6 (d t, 4 H, J = 7, 17 Hz); ^{19}F NMR ø 121.6 (m, 4 F), 120 (m, 4 F), 110.4 (m, 4 F); IR (neat) 3050, 1595, 1190, 1150 cm^{-1}.

Anal. Calcd for $C_{10}H_6F_{12}N_4O_8$: C, 22.32; H, 1.12; F, 42.36. Found: C, 23.92; H, 1.40; F, 42.63.

1,1-Dinitro-1H,2H,2H-perfluorooctane. In a manner similar to that described above, reaction of 1-nitro-1H,1H,2H,2H-perfluorooctane (1.5 g, 3.8

mmol) with tetranitromethane (3.1 g, 15.8 mmol) in methanol (45 mL) in the presence of potassium carbonate (1.2 g, 8.7 mmol) gave, after recrystallization from hexane/ether, 0.60 g (36%) of 1,1-dinitro-1H,2H,2H-perfluorooctane: mp 70-71.5 °C; IR (CH_2Cl_2) 3000, 1590, and 1100-1250 cm^{-1}; ^1H NMR (acetone-d_6) δ 6.96 (t, J = 6 Hz, 1 H) and 3.53 (dt, J = 16 and 6 Hz, 2 H).

Anal. Calcd for $C_8H_3F_{13}N_2O_4$: C, 21.93; H, 0.69; N, 6.39; F, 56.37. Analysis pending.

2,2,9,9-Tetranitro-1H,1H,3H,3H,8H,8H,10H,10H-perfluorodecane-1,10-diol. A solution of 1,8-dinitro-1H,1H,2H,2H,7H,7H,8H,8H-perfluorooctane (2.81 g, 8.03 mmol) and sodium carbonate (11.5 g, 108 mmol) in methanol (100 mL) was stirred at room temperature for 15 min. Tetranitromethane (12.0 g, 60.7 mmol) was added to the methanol solution, dropwise, and the mixture was stirred at room temperature for 18 h. *The mixture was diluted with* CH_2Cl_2 (500 mL), filtered and the yellow precipitate washed with CH_2Cl_2 (2 x 100 mL). The solid was dissolved in methanol (40 mL) and 37 % aqueous formaldehyde (25 mL) was added, and the solution was stirred at room temperature for 2 h. Then, the solution was brought to pH 6 by the slow addition of glacial acetic acid, and diluted with water (100 mL). This mixture was extracted with ether (2 x 100 mL) and the combined extracts were washed with water (2 x 50 mL), dried ($MgSO_4$), and concentrated to give a yellow solid. The solid was recrystallized (ether/hexane) to give 2.41 g (55%) of 2,2,9,9-tetranitro-1H,1H,3H,3H,8H,8H,10H,10H-perfluorodecane-1,10-diol as a white solid: mp 134-6 °C; ^1H NMR (acetone-d_6) δ 4.53 (s, 4 H), 3.75 (t, 4 H, J = 18 Hz); ^{19}F NMR ϕ 121.2 (m, 4 F), 110.8 (m, 4 F); IR (neat) 1575, 1130, 1120 cm^{-1}.

Anal. Calcd. for $C_{10}H_{10}N_4F_8O_{10}$: C, 24.11; H, 2.02; N, 11.25; F, 30.51. Found: C, 24.32; H, 2.08; N, 11.70; F, 30.50.

2,2,9,9-Tetranitro-1H,1H,3H,3H,8H,8H,10H,10H-perfluorodecane-1,10-diol was also prepared from 1,1,8,8-tetranitro-1H,2H,2H,7H,7H,8H-perfluorooctane and aqueous 37% formaldehyde, (80%): mp 130-133 °C.

2,2,11,11-Tetranitro-1H,1H,3H,3H,10H,10H,12H,12H-perfluorododecane-1,12-diol. A solution of 1,10-Dinitro-1H,1H,2H,2H,9H,9H,10H,10H-perfluorodecane (3.62 g, 8.08 mmol) and sodium carbonate (11.5 g, 108 mmol) in methanol (150 mL) was stirred at room temperature for 15 min. Tetranitromethane (12.0 g, 60.7 mmol) was added to the methanol solution, dropwise, and the mixture was stirred at room temperature for 18 h. The mixture was diluted with CH_2Cl_2 (500 mL), filtered and the yellow precipitate washed with CH_2Cl_2 (2 x 100 mL). The solid was dissolved in methanol (40 mL) and 37 % aqueous formaldehyde (25 mL) was added, and the solution was stirred at room temperature for 2 h. Then, the solution was brought to pH 6 by the slow addition of glacial acetic acid, and diluted with water (100 mL). This mixture was extracted with ether (2 x 100 mL) and the combined extracts were washed with water (2 x 50 mL), dried ($MgSO_4$), and concentrated to give a yellow solid. The solid was recrystallized (ether / hexane) to give 3.65 g (75%) of 2,2,11,11-tetranitro-1H,1H,3H,3H,10H,10H,-12H,12H-perfluorododecane-1,12-diol as a white solid: mp 152-4 °C; ^1H NMR (acetone-d_6): δ 4.60 (s, 4 H), 3.55 (t, 4 H, J = 17 Hz); ^{19}F NMR: ø 121.3 (m, 4 F), 119.6 (m, 4 F), 110.8 (m, 4 F); IR (thin film): 3460, 1575, 1125 cm^{-1}.

Anal. Calcd for $C_{12}H_{10}F_{12}N_4O_{10}$: C, 24.09; H, 1.69; F, 38.11; N, 9.37. Found: C, 24.56; H, 1.84; F, 37.81; N, 8.79.

2,2-Dinitro-1-hydroxy-1H,1H,3H,3H-perfluorononane. Potassium carbonate (7 mg, 0.05 mmol) was added to a solution of 1,1-dinitro-1H,2H,-2H-perfluorooctane (110 mg, 0.25 mmol) and 37% aqueous formaldehyde (2 mL) in methanol (5 mL) and the mixture was stirred at room temperature for 2 d. The reaction mixture was concentrated under reduced pressure, diluted with water, and extracted with diethyl ether (3x). The combined ethereal layers were washed with water and brine (2x), dried, filtered, and evaporated under reduced pressure to give a semi-solid residue. The residue was triturated with dichloromethane/hexane, cooled and filtered to give 65 mg (55%) of 2,2-dinitro-1-hydroxy-1H,1H,3H,3H-perfluorononane: mp 91-92 °; IR (CH_2Cl_2) 3350, 3050, 1590 and 1150-1250 cm^{-1}; ^1H NMR (acetone-d_6) δ 5.30 (m, exchanges with D_2O), 4.33 (s, 2 H) and 3.60 (t, J = 17 Hz, 1 H).

Anal. Calcd for $C_9H_5F_{13}N_2O_5$: C, 23.09; H, 1.08; N, 5.98; F, 52.76

Found: submitted for analysis.

2,2-Dinitro-1-hydroxy-1H,1H,3H,3H-perfluorotridecane. Potassium carbonate (0.52 g, 3.8 mmol) was added to a solution of 1-nitro-1H,1H,2H,2H-perfluorododecane (1.0 g, 1.7 mmol) in THF (10 mL) and methanol (32 mL). After 30 min, TNM (1.3 g, 6.6 mmol) was added dropwise over 15 min, and the mixture was stirred at room temperature for 18 h. The reaction mixture was diluted with dichloromethane (200 mL), filtered, and the solid washed with dichloromethane. The yellow solid was suspended in a solution of aqueous 37% formaldehyde (15 mL) and methanol (7 mL), and the mixture was stirred at room temperature for 1 d. The reaction mixture was acidified with glacial acetic acid and extracted with diethyl ether (3x). The combined ethereal layers were washed with water

and brine, dried, filtered and evaporated under reduced pressure to give a yellow solid. Recrystallization of this solid from chloroform gave 0.58 g (51%) of 2,2-dinitro-1-hydroxy-1H,1H,3H,3H perfluorotridecane: mp 124.5-126 °C; IR (thin film) 3550, 3050, 1590 and 1100-1300 cm^{-1}; ^{1}H NMR (acetone-d_6) δ 5.59 (m, exchanges with D_2O, 1 H), 4.63 (s, 2 H) and 3.82 (t, J =17 Hz, 2 H).

Anal. Calcd for $C_{13}H_2F_{18}O_5N_2$: C, 23.36; H, 0.75; N, 4.19

Found: C, 23.31; H, 0.68; N, 4.36.

Dimethyl 6,6,7,7,8,8,9,9-Octafluoro-4,4,11,11-tetranitrotetradecanedioate. A solution of methyl acrylate (1.1 g, 12.8 mmol) in 8:1 dioxane/water (17 mL) was added over 45 min to a solution of 1,1,8,8-tetranitro-1H,2H,2H,7H,-7H,8H-perfluorooctane (1.0 g, 2.3 mmol) and Triton-B (1.0 mL) in 5:1 dioxane/water (77 mL) at 60 °C. After 21 h at 60 °C, a second portion of methyl acrylate (0.8 g, 9.3 mmol), dissolved in dioxane (8 mL), was added and the mixture was stirred at 60 °C for an additional 6 h and at room temperature for 2 d. The mixture was diluted with dichloromethane and poured over crushed ice, water and conc. HCl (3 mL). The organic layer was separated and the aqueous layer was extracted with dichloromethane. The combined organic layers were washed with water (2x), 10% aqueous sodium carbonate (2x), and brine (2x), dried, filtered and evaporated under reduced pressure to give a brown semi-solid. The residue was triturated with diethyl ether, cooled and filtered to give 0.60 g (43%) of dimethyl 6,6,7,7,8,8,9,9-octafluoro-4,4,11,11-tetranitrotetradecanedioate: mp 132-133 °C (acetone/water); IR (CH_2Cl_2) 2950, 1750, 1590, and 1100-1300 cm $^{-1}$; ^{1}H NMR (acetone-d_6) δ 4.01 (t, J = 17 Hz, 4 H), 3.71 (s, 6 H), 3.15 (t, J = 6

Hz, 4 H) and 3.78 (t, J = 6 Hz, 1 H); ^{19}F NMR ($CDCl_3$) ϕ 110.4 (4 F) and 121.2 (4 F).

Anal. Calcd for $C_{18}H_{14}F_8N_4O_{12}$: C, 31.48; H, 2.37; N, 9.18; F, 24.90. Found: C, 31.27; H, 2.94; N, 9.05; F, 24.72.

6,6,7,7,8,8,9,9-Octafluoro-4,4,11,11-tetranitrotetradecanedioic Acid. A solution of dimethyl 6,6,7,7,8,8,9,9-octafluoro-4,4,11,11-tetranitrotetradecanedioate (0.21 g, 0.34 mmol) in concentrated hydrochloric acid (5 mL), water (5 mL), and dioxane (7.5 mL) was refluxed for 5 h. The mixture was cooled to 0 °C and the solid was filtered, washed with water, and dried to give 0.19 g (94%) of the diacid as an off-white solid. Recrystallization from ethanol gave white crystals: mp 187–188 °C; ^{1}H NMR (acetone-d_6) δ 3.98 (t, J = 18 Hz, 4 H), 3.05 (m, 4 H), 2.62 (m, 4 H); ^{19}F NMR ϕ 110 (m, 4 F), 120.0 (m, 4 F); IR (CH_2Cl_2) 3600–2800, 1760, 1575 cm^{-1}.

Anal. Calcd for $C_{16}H_{10}F_8N_4O_{12}$: C, 28.88; H, 2.42; F, 26.10; N, 9.62. Found: C, 29.62; H, 2.53; F, 20.43; N, 9.17.

Dimethyl 6,6,7,7,8,8,9,9,10,10,11,11-Dodecafluoro-4,4,13,13-tetranitrohexadecanedioate. A solution of 1,1,10,10-tetranitro-1H,2H,2H,9H,9H,10H-perfluorodecane (1.02 g, 1.90 mmol), methyl acrylate (1.43 g, 16.6 mmol), and methanolic Triton B (0.386 mL, 1.9 mmol) in dioxane (30 mL) and water (10 mL) was heated at 60 °C for 20 h. The mixture was diluted with water (100 mL), acidified with 20% hydrochloric acid, and extracted with methylene chloride (2 × 50 mL). The combined methylene chloride layers were washed with water, dried (magnesium sulfate), and concentrated. The brown residue was recrystallized from methanol to give the 0.21 g (16%) of dimethyl 6,6,7,7,8,8,9,9,10,10,11,11-dodecafluoro-4,4,13,13-tetranitro

hexadecanedioate.: mp 138.5 139 °C; ^{1}H NMR δ 4.94 (t, J = 18 Hz, 4 H), 3.72 (s, 6 H), 3.10 (m, 4 H), 2.80 (m, 4 H); IR (CH_2Cl_2) 1750, 1580 cm^{-1}.

Anal. Calcd for $C_{18}H_{18}F_8N_2O_{12}$: C, 30.43; H, 2.55; F, 32.11; N, 7.89. Found: C, 29.64; H, 2.57; F, 38.96; N, 6.94.

Dimethyl 4,11-Dinitro-6,6,7,7,8,8,9,9-octafluorotetradecanedioate. A solution of 1,8-dinitro-1H,1H,2H,2H,7H,7H,8H,8H-perfluorooctane(0.584 g, 1.68 mmol), methyl acrylate (0.29 g, 3.4 mmol), and 1,8 diazabicyclo-(5.4.0.)undec-7-ene (0.26 g, 1.7 mmol) in acetonitrile (50 ml) was stirred at ambient temperature for 16 h. The solution was diluted with water (50 ml) and the aqueous layer was acidified with 20 % HCl and extracted with methylene chloride (3 x 50 ml). The combined organic extracts were washed with water (2 x 50 ml), dried over magnesium sulfate, and concentrated. The brown residue was chromatographed on silica gel with methylene chloride to give 0.323 g (37 %) of dimethyl 4,11-dinitro-6,6,7,7,8,8,9,9-octafluorotetradecanedioate: mp 76-78 °C (ethanol); ^{1}H NMR ($CDCl_3$) δ 4.92 (m, 2 H), 3.57 (s, 6 H), 2.60 - 2.20 (m, 12 H); ^{19}F NMR σ 116.0 (m, 2 F), 124.8 (m, 2 F); IR ($CHCl_3$) 1750, 1560, 1260 cm^{-1}.

Anal. Calcd for $C_{18}H_{20}F_8N_2O_8$: C, 36.93; H, 3.87; N, 5.39; F, 29.21. Found: C, 37.29; H, 3.93; N, 5.35; F, 29.00.

Dimethyl 4,11-Bis(2-methoxycarboxyethyl)-4,11-dinitro-6,6,7,7,8,8,-9,9-octafluorotetradecanedioate. A solution of 1,8-dinitro-1H,1H,2H,2H,-7H,7H,8H,8H-perfluorooctane (0.10 g, 0.30 mmol), methyl acrylate (0.11 g, 1.2 mmol), and 1,8 diazabicyclo(5.4.0.)undec-7-ene (0.09 g, 0.60 mmol) in acetonitrile (5 ml) was stirred for 2 h at room temperature. The solution was diluted with water (25 ml), acidified with 20 % HCl, and

extracted with methylene chloride (3 × 20 ml). The combined methylene chloride extracts were washed with water, dried, and concentrated. The brown oil was dissolved in warm methylene chloride (10 ml) and hexane was added to cloud point. Slow cooling gave 0.095 g (46 %) of dimethyl 4,4-bis(2-methoxycarbonylethyl)-1,1-dihydro-6,6,7,7,8,8,9,9-octafluoro tetradecanedioate: mp 126-8 °C (methylene chloride/hexane); ^{1}H NMR (CDCl$_3$) δ 3.68 (s, 6 H), 3.0 - 2.0 (m, 20 H); ^{19}F NMR φ 111.0 (m, 4 F), 124.4 (m, 4 F); IR (CH$_2$Cl$_2$) 1750, 1560, 1250, 1090 cm^{-1}.

Anal. Calcd for C$_{24}$H$_{30}$F$_8$N$_2$O$_8$: C, 41.62; H, 4.66; N, 4.05; F, 21.95. Found: C, 41.86; H, 4.70; N, 4.01; F, 21.69.

REFERENCES

1. Fluorochem, Inc. Report No. 0Rh 2 9. *Research in Energetic Compounds*, February 1987.

2. Farnum, D. G.; Mostashari, A. J. *Org. Photochem. Syn.* 1971, *1*, 79.

3. (a) Wolfe, S.; Hasan, S. K.; Campbell, F. R. *J. Chem. Soc. D.* 1970. 1420. (b) Paquette, L. A.; Drevasel, J.; Chassey, K. L. *J. Am. Chem. Soc.* 1986, *108*, 512. (c) Caputo, J. A.; Fuchs, R. *Tetrahedron Lett.* 1967, 4729. (d) Piatak, D. M.; Herbst, G; Wicha, J.; Caspi, E. *J. Org. Chem.* 1969, *34*. 116. (e) Ayres, D. C.; Hossain, A. M. *J. Chem. Soc., Chem. Commun.* 1972, 428.

4. (a) Liotta, R.; Hoff, W. S. *J. Org. Chem.* 1980, *45*, 2887. (b) Deno, N. C.; Greigger, B. A.; Messer, L. A.; Meyer, M. D.; Stroud, S. S. *Tetrahedron Lett.* 1977, 1703. (c) Pyatnitskii, R. *Russ. Chem. Rev.* 1976, *45*, 762.

5. *Klein, H.; Steinmetz, A. Tetrahedron Lett.* 1975, 4249

6. Miller, D. B.; Flanagan, P. W.; Shechter, H. *J. Am. Chem. Soc.* 1972, *94*, 3912, 3919 and *J. Org. Chem.* 1976, *41*, 2112.

7. (a) Wiberg, K. B.; Lavanish, J. M. *J. Am. Chem. Soc.* 1966, *88*, 5272. (b) Stevens, I. D. R.; Frey, H. M. *Proc. Chem. Soc.* 1964, *144*.

8. *Smith, J. A.; Shechter, H.; Bayless, J.; Friedman, L. J. Am. Chem. Soc.* 1965, *87*, 659.

9. (a) Wiberg, K.; Lampman, G. M.; Ciula, R. P.; Connor, D. S.; Schertler, P.; Lavanish, J. *Tetrahedron* 1965, *21*, 2749. (b) Wiberg, K. B.; Lampman, G. M. *J. Am. Chem. Soc.* 1966, *88*, 4429.

10. Perlmutter, H. D.; Knapp, P. S. *J. Org. Chem.* 1967, *32*, 2349.

11. Corey, E. J.; Samuelsson, B.; Luzzio, F. A. *J. Am. Chem. Soc.* 1984, *106*, 3682.

12. Vasin, V. A.; Bolusheva, I. Y.; Tanaseichek, B. S. *Zh. Org. Khim.* 1986, *22*, 670.

13. Cripps, H. N.; Williams, J. K.; Sharkey, W. H. *J. Am. Chem. Soc.* 1959, *81*, 2723.

14. Hall, H. K.; Blanchard, E. P.; Cherkofsky, S. C.; Sieja, J. B.; Sheppard, W. A. *J. Am. Chem. Soc.* 1971, *93*, 110.

15. (a) Barnes, M. W. *J. Org. Chem.* 1976, *41*, 633. (b) Corey, E. J.; Estreicher, H. *Tetrahedron Lett.* 1980, *21*, 1117.

16. Pfister, J. R.; Wymann, W. E. *Syn.* 1983, 38.

17. Shioiri, T.; Ninomiya, K.; Yamada, S. *J. Am. Chem. Soc.* 1972, *94*, 6203.

18. Gilbert, K. E.; Borden, W. T. *J. Org. Chem.* 1979, *44*, 659.

19. (a) Bull, J. R.; Jones, E. R. H.; Meakens, G. D. *J. Chem. Soc.* 1965, 2601. (b) Fieser, L. F. Doering, W. von E. *J. Am. Chem. Soc.* 1946, *68*, 2252. (c) Riebsomer, *J. L. Chem. Rev.* 1945, *36*, 157.

20. (a) Fujii, T.; Tashiro, M.; Ohara, K.; Kumai, M. *Chem. Pharm. Bull.* 1960, 266. (b) White, E. H. *J. Am. Chem. Soc.* 1955, *77*, 6008, 6011, 6014.

21. Shoppe, C. W.; Sty, J. C. P. *J. Chem. Soc.* 1959, 345.

22. Corey, E. J.; Suggs, J. W. *Tetrahedron Lett.* 1975, 2647.

23. Fieser, L. F.; Fieser, M. "Reagents for Organic Synthesis", pp 147-147, John Wiley and Sons, New York, 1967.

24. Brown, H. C.; Garg, C. P. *J. Am. Chem. Soc.* 1961, *83*, 2952.

25. Bowden, K.; Heilbron, I. M.; Jones, E. R. H.; Weedon, B. C. L. *J. Chem. Soc.* 1946, 39.

26. (a) Zimmerman, H. E.; Hancock, K. G.; Licke, G. C. *J. Am. Chem. Soc.* 1968, *90*, 4892. (b) Kahr, K.; Berther, C. *Chem. Ber.* 1960, *93*, 132.

27. Lee, G. A.; Freedman, H. H. *Tetrahedron Lett.* 1976, 1691.

28. Buckley, T. F.; Rapoport, H. *J. Am. Chem. Soc.* 1982, *104*, 4446.

29. Avram, M. A.; Nenitzescu, C. D.; Maxim, M. *Chem. Ber.* 1957, *90*, 1424.

30. (a) Weinstock, T. *J. Org. Chem.* 1961, *26*, 3511. (b) Beard, C.; Burger, A. *J. Org. Chem.* 1962, *27*, 1647 and *1961*, *26*, 2335. (c) Wheeler, T. N.; *ibid*, J. J. *Org. Chem.* 1987, *52*, 4875 and reference 7 therein.

31. Ericksson, J. L.; Collins, F. E.; Owen, B. L. *J. Org. Chem.* 1966, *31*, 480.

32. (a) Fluorochem, Inc. Report No. ONR-2-7, *Research in Energetic Compounds*, Appendix A, January 1985. (b) Anderson, A. G., Jr.; Lok, K. *J. Org. Chem.* 1972, *37*, 3953.

33. Ewern, D.; Omura, K. *Tetrahedron* 1978, *34*, 1651.

34. Terent'ev, A. P.; Gusar, N. I. *Zhur. Obshch. Khim.* 1965, *35*, 125.

35. Smith, D. R.; Maienthal, M.; Tyrton, J. *J. Org. Chem.* 1952, *17*, 294.

36. *Gajewski, J. J.; Burke, L. P. J. Am. Chem. Soc.* 1972, *94*, 8865.

37. Archibald, T. G.; Baum, K. "Research in Energetic Compounds" Fluorochem Report No ONR-2-6, January 1984.

38. Archibald, T.G.; Tzeng, D. D.; Bonzu, F. O.; Baum, K. "Studies of Cycloaddition Reactions of Tetranitroethylene and Preparation of Trinitroazetidine" Fluorochem Report on Contract DAAK10-85-C-0076, March 1986.

39. Willer, R., Morton Thiokol, Private communication.

40. Gillardi. R. NRL, Private communication.

41. Gaertner, V. R. *J. Org. Chem.* 1967, *32*, 2972.

42. Okutani, T.; Kaneko, T.; Masuda, K. *Chem. Pharm. Bull.* 1974, *22*, 1490.

43. Feuer, H.; Leston, G.; Miller, R.; Nielson, A. T. *J. Org. Chem.* 1963, *74*, 3664

44. Moffett, R. B. *Org. Syn.* 1963, *IV*, 652.

45. Carpino, L. A.; Sau, A. C. *J. Chem. Soc., Chem. Comm.* 1979, 514.

46. Kambe, S.; Yasuda, H. *Bull. Chem. Soc. Jpn.* 1966, *39*, 2549.

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